Master Thesis, Department of Geosciences

Fate of De-icers in Soil and Ground Water

A case study at Oslo International Airport, Gardermoen

Junaid Riaz

UNIVERSITY OF OSLO

FACULTY OF MATHEMATICS AND NATURAL SCIENCES

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Acknowledgment

In the name of Allah, Most Gracious, Most Merciful.

All praises to Allah who is *Al-Aleem* (all knowing) for granting me the opportunity to successfully pursue Masters degree in a world leading university. Thanks to Allah as there is neither progress nor might except through Him. Peace be upon the greatest teacher of humanity and mankind, the Holy Prophet Muhammad (Peace be upon Him).

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My sincere appreciation goes to all my friends who have encouraged me and supported me throughout my stay in Norway. Finally, it was the continuous support of my parents and my sisters that served the main driving force and motivation. I could not have done this without their help and support.

I wish and pray that my research may play a vital role in reducing the impacts of upcoming global water crises.

Junaid Riaz

Abstract

Water scarcity is a striking issue all over the world because of increased water utilization resulting from growing population. Prevention and sustainable usage of ground water is the keen concern of every government these days. Possible preventive measures are adopted on all the grounds where there are chances of depletion of water resources. For this reason all major operational projects abide by certain rules to minimise any potential damage they can cause to the environment in general, and water in particular. De-icers are widely used not only to keep roads and airport runways open for winter operation, but also to prevent accidents. To prevent corrosion, organic based de-icers are the preferred choice at airports. Formate and acetate based products are used for runways while propylene glycol is used as anti-freeze on the airplane itself. De-icers are a potential source of contamination at the Oslo International Airport (OSL) which lies above the largest aquifer of Norway.

This study is based on the column elution and batch experiments performed on OSL runway soil samples and Glomma river fluvial deposits taken from Elverum municipality. The natural degradation along with sorption due to TOC has been considered to calculate the over all retardation factor for formate. Contaminant velocities have been calculated to measure the attenuation process within the soils. The columns have been eluted on different flow rates to observe changes in degradation accordingly. Chloride is used as a non reactive tracer electrolyte which behaved as the control for the column experiments. Batch experiments played a vital role in understanding the natural tendency of both soil samples to degrade formate. Nitrate was added to both sets of experiments as a nutrient source to enhance the microbial activity. The retardation factor of formate has been calculated as 1.1 and 1.3 in Elverum and OSL soil samples, respectively. EC and COD measurements were considered as parameters to measure degradation/sorption. AAS was used to measure Fe and Mn concentrations and their presence in the column outlets and in the batch experiments indicates the redox processes in both experiments. Detailed analysis of the findings from this study suggests that providing a good air supply and nutrients formate can be completely degraded in the unsaturated zone before it reaches the aquifer.

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List of abbreviations

AAF	Aircraft Anti-Icing Fluid
AAS	Atomic Absorption Spectrophotometer
ADF	Aircraft Deicing Fluid
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DOT	Department of Transportation
EC	Electronic Conductivity
ELV	Elverum Municipality
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration of United States
FAO	Food and Agricultural Organization of United Nations
NGU	Norges Geologiske Undersokelse
OSL	Oslo International Airport, Gardermoen
PG	Propylene Glycol
TC	Total Carbon
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
UNESCO	United Nations Educational, Scientific and Cultural Organization

Chapter 1: Introduction

1.1. Ground water

1.1.1. Importance of ground water

The global water demand has increased rapidly in line with the population growth. In some regions of the world like Africa and Middle East; groundwater is the major source of water supply for household and industrial purposes. In these regions, the main use of groundwater resource is for irrigation purposes which have improved the livelihood for millions of people in the global scale (Shah et al., 2007). The popularity of groundwater can be explained by the reliability and flexibility of access to water that for instance irrigation canals cannot provide (FAO, 2005; Seibert et al., 2010). Also, from a drinking water supply perspective, the general quality of groundwater is much better than surface water or water running through irrigation canals (Seibert et al., 2010).

1.1.2. Distribution of ground water

97% of the total water present on earth is salty and is present in the oceans. The remaining 3% is fresh water out of which almost 2/3 parts is in the form of glaciers or ice in the hilly areas and arctic regions. The remaining 1/3 parts is fresh water. 98% of this fresh water is the ground water. The remaining is covered by lakes and rivers. The main available source of fresh water to the world is ground water available in the form of sub surface aquifers (Bouwer, 1978) as cited in (Bouwer, 2002).

1.1.3. Usage of ground water in Norway

In Norway about 15 % of water supply is based on groundwater. This is rather low compared with many other European countries, such as Denmark, Austria and Iceland, which use groundwater for more than 95 % in their water supply. Groundwater in Norway, compared with surface water, contains relatively little organic matter, but elevated values for hardness, electrical conductivity and pH. In addition, groundwater has usually a stable temperature and quality throughout the year. However, the use of groundwater for water supply is not without problems. Elevated contents of radon, fluoride, iron and manganese are problematic in many bedrock wells,

while low values for pH and alkalinity, and elevated contents of iron and manganese are common problems in wells in unconsolidated sediments. (NGU, 2008)

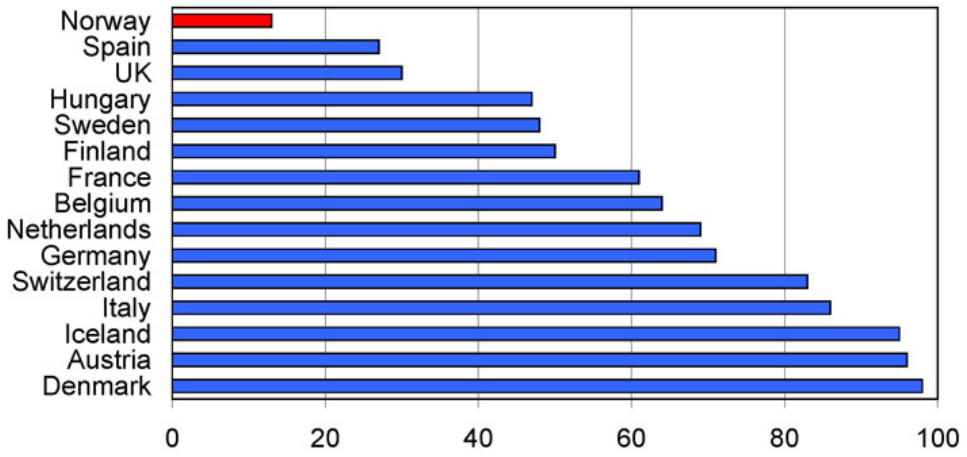

Figure 1.1: Use of Ground water in Europe, as a percentage of total (NGU, 2008).

1.1.4. Sources of ground water contamination

The extensive use of groundwater resources can result in depletion and contamination of groundwater. The impact of such deterioration can significantly be realized gradually (Das et al., 2002). Groundwater contamination can create complex processes within the ground water systems and may lead to serious health impacts. Groundwater contaminants include nitrogenous compounds e.g. ammonia and nitrates, sulphates, phenols and heavy metals (UNESCO, 2004).Groundwater contamination can result from infiltration of untreated storm water, municipal waste water spills and other industrial waste water intrusion into the aquifer. Anthropogenic activities play a vital role in groundwater contamination, for instance agricultural practices and waste handling can contaminate the groundwater (Moody, 1996). Mine dewatering and irrigation from waste water may result in contamination of groundwater (Muhammad et al., 2011). Industrial effluents result in accumulation and precipitation of heavy metals in groundwater e.g. Iron and Manganese. Heavy metals are naturally occurring elements having atleast 5 times the specific gravity of water. Other sources of heavy metals are weathering of bed rock, and leaching from mines etc. All heavy metals are toxic to life but some may be required in low quantities e.g. Iron, Magnesium, Calcium and Manganese (Salem et al., 2004). Iron and Manganese are present in anoxic conditions within the groundwater (Ebermann et al., 2010).

Higher concentrations of Iron and Manganese can cause coloring of water but do not cause any serious threat to human life (Tredoux et al., 2004)

1.2. Problem Description

1.2.1. De-icers

De-icers are the organic or inorganic chemicals in nature, naturally occurring or synthetic which are used during the winter seasons to remove ice from the road or runway surfaces and also from the mechanical parts of heavy traffic and airplanes which are exposed to snow and cold outside temperatures. With respect to the functioning of airports located in the cold climates, de-icers mean the chemical substances which are used on runways and taxiways to clear off the snow, prevent further accumulation of snow and sprayed over the airplanes to make their surfaces ice free (Klecka et al., 1993)

Aircraft de-icing usually follows runway de-icing. It serves the purpose of preventing the accumulation of snow or ice on the deiced surfaces of the aircraft. It is applied either immediately before the take-off particularly during severe weather conditions, or during overnight parking. Antiicing is accomplished by applying Type IV anti-icing fluid (AAF) or aircraft de-icing fluids (ADF) to clean (i.e., icefree) aircraft surfaces. The exact composition of ADF or AAF varies according to the proprietary formulations but generally, chemicals other than glycol make up only 1 to 5% of fluid (USDOT, 1992).

1.2.2. Need for application of deicers

Snow or ice on the runway or aircraft's surfaces can result in serious accidents. USAir Flight 407 crashed on takeoff at New York's Laguardia Airport during a winter storm in March 1992. Twenty-seven passengers and crew were killed in this accident. In another incidence a Scandinavian Airlines System (SAS) flight 751 suffered a similar accident in 1991 while flying from Stockholm to Copenhagen. The accumulation of ice on the wings was believed to be the cause of the accident. With similar accidents in view, the Federal Aviation Administration (FAA) imposed more stringent requirements on de-icing activities to increase the margin of safety for air travel during snow and ice conditions. These new protocols are grounded in the

"clean aircraft concept", which requires that aircraft surfaces must be free of snow and ice before departure and imposes time limits (holdover time) between the application of de-icing fluids and aircraft departure. (Switzenbaum et al., 1999)

1.2.3. Types of deicers

a) Runway and Aircraft deicers:

The runway deicers also known as pavement deicers serve to break the bond holding ice and snow to the surfaces of runways and taxiways, thus facilitating mechanical removal of ice and snow to maintain an adequate friction between aircraft tires and the runway. Pavement de-icing is generally the responsibility of the airport operating staff. Residual pavement de-icing materials (PDMs) left on the runway provide anti-icing protection. Liquid PDMs are primarily applied in anticipation of major de-icing events whereas solid PDMs are primarily applied to existing ice and snow. Solid PDMs include sodium acetate, sodium formate, and urea; liquid PDMs include potassium acetate and potassium formate. (Switzenbaum et al., 1999)

Aircraft de-icing is applied to larger aircrafts to keep the aircraft surfaces clear of any ice. Various types of ADFs are available such as Type I, type II, type III and type IV. These types differ in their composition. However, the major components of ADFs include ethylene or propylene glycol and some additional thickening agents (present in ADFs types II, III and IV). The thickening agents tend to stick to the surface of the aircraft therefore providing longer holdover times which result in anti-icing effect in addition to the usual de-icing. (Switzenbaum et al., 1999)

b) Deicers according to their composition:

The deicers which are applied nowadays at various airports around the world are based on glycols or organic salts. An overview over the different products is given below:

i) **Glycols:**

Glycols are organic compounds in the alcohol class. Alcohols, as a rule, are polar molecules which tend to have high boiling points, therefore, serve as excellent freezing point depressants. Alcohols up to 3 carbons in length are completely miscible in water. Ethylene glycol and

propylene glycol are the two most widely used aircraft de-icing agents in use nowadays. Diethylene glycol, commonly used in Europe, is seldom used in North American de-icing applications. (Aherns,2008)

a) **Ethylene glycol:**

Ethylene glycol ($HOCH_2CH_2OH$) generally is the major component of aircraft deicers, making up 30 to 70% of the solution along with propylene glycol. Either alone or in combination, these glycols, are used on runways and airport roadways.Ethylene glycol has been the standard for antifreezes and deicers for years because of its low cost (Switzenbaum et al., 1999). It is a colorless, slightly viscous liquid with a freezing point of -13 $^{\circ}$C, and it can lower the freezing point of water to about -50 $^{\circ}$C, depending on dilution. Even its small concentrations in the drinking water can cause nervous break down and later death of the organism ingesting it. (Aherns,2008)

b) **Propylene glycol:**

Propylene glycol is a colorless, viscous, hygroscopic and nearly an odorless liquid. In addition to its use as an aircraft de-icing fluid, propylene glycol is also widely used as a chemical intermediate, a humectants (dessicant) in foods, an emollient (solvent) in cosmetic and pharmaceutical creams, a latex paint additive, an inhibitor of fermentation and mold growth and as a plasticizer for resins and paper .(Aherns,2008) Some other uses include its use as a non-toxic antifreeze in breweries and dairy establishments, in heat exchangers and in the vapor form as an air sterilizer for hospitals and public buildings.

Chemically the structure of propylene glycol is similar to ethylene glycol except that propylene glycol contains a third carbon atom as shown in figure 1.2. Other designations for the material which are derived from its chemical structure or trade uses include 1,2-dihydroxypropane, Dowfrost, 2-hydroxypropanal, methylethylene glycol, methyl glycol, monopropylene glycol, 1,2- propanediol, propane-1,2-diol, 1,2-propylene glycol, Sirlene, Solar Winter Ban and trimethyl glycol (Aherns,2008)

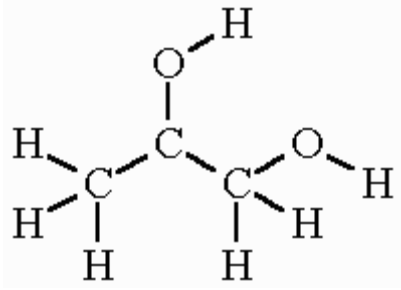

Figure 1.2: Chemical structure of propylene glycol

Today, most ADAF consist of propylene glycol (1,2-propanediol), diluted to 50–75% application concentration by water. Depending on the airport facilities, between 20% and 60% of the applied ADAF are diffusively spread to unpaved surfaces due to wind drift during application or shear off the airplane during takeoff for example (EPA, 2000; Novak et al., 2000; Breedveld et al., 2002).

Propylene glycol is not currently listed as a hazardous material by any federal or state agencies.(EPA, 2000)

ii) Organic salts:

a) Potassium formate:

Potassium formate (HCOOK or CHKO2) is a liquid pavement de-icing chemical which is in use at many airports around the world. While more expensive than conventionally used PDMs, the material has a much lower environmental impact, and could greatly reduce the costs associated with the collection and treatment of runoff. Potassium formate is manufactured by HydroAgri under the trade name Aviform L50 (Switzenbaum et al., 1999)

It is a colourless crystal deliquescent as it can absorb moisture from the air and can form a wet solid or a solution. It is usually in solid state having a density of 1.91 g/cm^3. It has a molecular weight of 84.12 grams and a melting point of 167 ^{o}C (Aherns, 2008)

b) **Potassium acetate:**

Potassium Acetate is clear, odorless, and is an easy-handling solution. The unique features and benefits of Potassium Acetate make it an ideal alternative to conventional ice melt applications It is comparatively less toxic and it has a very low biological oxygen demand (BOD) rate and contains no phosphates or urea. The lower the BOD rate, the quicker it decomposes into environmentally safe components (Aherns,2008)

c) **Urea:**

Urea is a compound with the chemical formula $(NH_2)_2CO$. It is found in nature (in our urine) and is also made artificially. It has a very high nitrogen content, and is most often used as a nitrogen-release fertilizer. While urea has many other uses, it is commonly used as a deicer

Urea has a high biochemical oxygen demand which means that as it degrades, it binds up the dissolved oxygen in the water and decreases the available oxygen to the organisms. As this compound dissolves in water, it releases nitrogen into the water, accelerating the growth of algae blooms, eutrophication and further cutting off the oxygen to other microbes and living organisms generating a "deadzone", where there is no dissolved oxygen to support life. (Aherns,2008)

1.2.4. Current Usage of Deicers

Each year large quantities of propylene glycol and ethylene glycol based ADFs are used to de-ice aircrafts On the average, it takes 3000 to 4000 liters of ADF to deice a large commercial aircraft (EPA, 1995). According to Betts (1999), a medium sized airport may use over 1,000,000 liters of fluid over the entire winter season. In addition, urea and acetate/formate-based runway deicers are in widespread use at most northern tier airports.

Environmental Protection Agency of United States (EPA) (2000) estimated an annual use of airplane de-icing/anti-icing fluids (ADAF) in the whole US to be at least 140,000 tons. According to the estimates a single mid-sized airport may use up to 10,000 tons ADAF annually to ensure safe transportation. Mean annual use in Germany is estimated to be about 5000 tons (Theloke et al., 2000).

1.2.5. Effects of deicers on natural environment:

The liquid water produced as a result of de-icing contains the de-icing chemicals. This water along with the de-icing chemicals can then enter surface water and pollute the environment. Secondly, it can stay in the soil as surface water or underground water for a short or longer period thus causing its effects on the soil. From the soil it can be eventually be absorbed by plants and can consequently affect plant growth.

The de-icing chemicals can lead to changes in the soil's physical, chemical and biological properties. For example, land degradation such as soil sealing and land salinization may emerge under these circumstances resulting in destabilization of aggregate and reduction of infiltration (Switzenbaum et al., 1999)

De-icing chemicals enter surface water and underground water via infiltration. They can alter water density by adding chemical load, consume large quantity of dissolved oxygen and then change the physical and ecological properties of water bodies. De-icing chemicals affect underground water mainly by polluting drinking water resulting in altered taste and higher salinity. This water, if used for drinking purposes, can result in some diseases, e.g. hypertension (Serrano & Gaxiola, 1994)

Organic material input to soils and aquifers originates from natural sources like moors or forest floors as well as from human activity related or accidental pollution. An anthropogenic organic carbon source just recently considered is the input of de-icing chemicals and its additives during winter-condition airport operation (Kent et al., 1999; EPA, 2000; French et al., 2001).

The environmental risk of ADF or AAF is generally believed to be as a result of the high biological oxygen demand during ADF/AAF biodegradation in streams and rivers receiving airport run-off (Kent et al., 1999) and the toxicity of ADF/AAF additives (Cancilla et al., 1997; Corsi et al., 2003).

Revised FAA protocols (FAA, 1992) have increased the quantities of de-icing fluids used by U.S. airlines and airports. This increase in de-icing activity, along with the increased air traffic in the recent decades, has resulted in greater quantities of de-icing fluid being entrained in airport runoff. (Switzenbaum et al., 1999)

Studies conducted at Gardemoen Airport in Norway have suggested that the de-icing chemicals used during the winter season are potential pollutants for the groundwater underneath the new main airport of Norway as there degradation may result in redox processes resulting in increased solubility of Mn and Fe in the aquifer. (French et al., 2001)

1.2.6. Natural Degradation and transport:

Degradation rates, retardation and residence times give an idea whether the contaminnat can reach the aquifer via unsaturated zone or not. A sandy soil has low biomass or low carbon contents and it is less efficient in biodegradation. Microbeal biomass most likely lies in the top soil and decrease with the depth resulting in lower biodegradation as we move down in the unsaturated zone (Webster et al,.1985) as cited in (French et al., 1999)

Sandy soils have mode hydraulic conductivity as compared to silty and loamy soils resulting in higher residence times for fine soils.(Bouwer, 2002)

Microbial activity is considered the key to natural pedogenic processes induced by reduction/ oxidation (redox) processes (Chadwick and Graham, 2000). In the absence of dissolved oxygen or nitrate, (hydr) oxides of iron and manganese may act as terminal electron acceptors during the anaerobic microbial decomposition of organic compounds (e.g., Lovley, 1997; Christensen et al., 2000). Aerobic biodegradation of propylene glycol has been demonstrated in batch or microcosm experiments (e.g., Klecka et al., 1993; Shupack and Anderson, 2000) at temperatures as low as −2 °C and has also been reported for field sites (French et al., 2001).

Alteration in the chemical properties of water present in the soil can give information about sediments tendency to degrade the contaminant.Fe and Mn can act as electron acceptors when redox conditions are dominant.(Appelo and Postma, 1996)

Propylene glycol is also degraded under anaerobic conditions (Kaplan et al., 1982). In studies of propylene glycol biodegradation in soil materials using open soil pans (Bausmith and Neufeld, 1999) and saturated sand columns (Bielefeldt et al., 2002), a decline of propylene glycol concentration was observed, but metabolites were not monitored. A number of studies have been conducted in aqueous solutions that illustrated pathways and kinetics of propylene glycol

degradation during anaerobic wastewater treatment of de-icing chemicals (Veltman et al., 1998; Schoenberg et al., 2001; Seok and Komisar, 2003).

Propylene glycol is supposed to be initially fermented via propionaldehyde to equi molar amounts of propionate and 1-propanol, with the latter usually converting quickly to propionate as well. Propionate is then further degraded to acetate, methane and carbon dioxide. (Mericas et al. 1994)

A similar study using lysimetric trench was conducted by (French et al., 1999) at OSL showing no degradation in Propylene glycol (PG) and the retardation factor for acetate was calculated as 1.24.

Table 1.1: Retardation factors calculated by (French et al., 1999)

Substance	Rf
Acetate	1.24
PG	1.01

Iron and Manganese Reactions**:**

The general reactions of Fe and Mn within an aquifer are given as

$$Fe^{+2} + 3H_2O = Fe(OH)_3 + 3H^+ + e^- \quad (1.1)$$

The above equation can be splitted into following two equations (1.2 and 1.3)

$$Fe+2 = Fe^{+3} + e^- \quad (1.2)$$

$$Fe^{+3} + 3OH- = Fe(OH)\,3 \quad (1.3)$$

$$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^- \quad (1.4)$$

Table 1.2: Electron donor reaction for deicing chemicals. (Klonowski et al., 2007)

e^- -donor	**Mineralization reactions**
Propyleneglycol	$C_3H_8O_2 + 4\ H_2O \rightarrow 3\ CO_2 + 16\ H^+ + 16\ e^-$
Formate	$CHO_2^- \rightarrow\ CO_2 + H^+ +\ 2e^-$
Acetate	$C_2H_3O_2^- + 2\ H_2O \rightarrow 2\ CO_2 + 7\ H^+ + 8\ e^-$

The substances tend to oxidize releasing electrons resulting in a reducing environment.Formate releases 2 electrons on its degradation.

Table 1.3: Electron acceptor reactions (Klonowski et al., 2007)

e^- -acceptor	**Reaction**
Oxygen	$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$
Nitrate	$2NO_3^- + 12\ H^+ + 10\ e^- \rightarrow N_2 + 6\ H_2O$
Manganese	$Mn^{4+} + 2\ e^- \rightarrow Mn^{2+}$
Iron	$Fe^{3+} +\ e^- \rightarrow Fe^{2+}$
Sulfate	$SO_4^{2-} + 10\ H^+ + 8\ e^- \rightarrow H_2S + 4\ H_2O$
Methanogenisis	$CO_2 + 8\ H^+ + 8\ e^- \rightarrow CH_4 + 2\ H_2O$

These substances get reduced after accepting electrons from the electron donors. Table 1.3shows the electron donors in order of their availability. In anoxic conditions first nitrate will be reduced.after that Mn and Fe will behave as electron acceptors.

Adsorption, absorption and ion exchange are the three sorption factors that can retards the solute movement through some aquifer as suggested by (Appelo and Postma 2005).

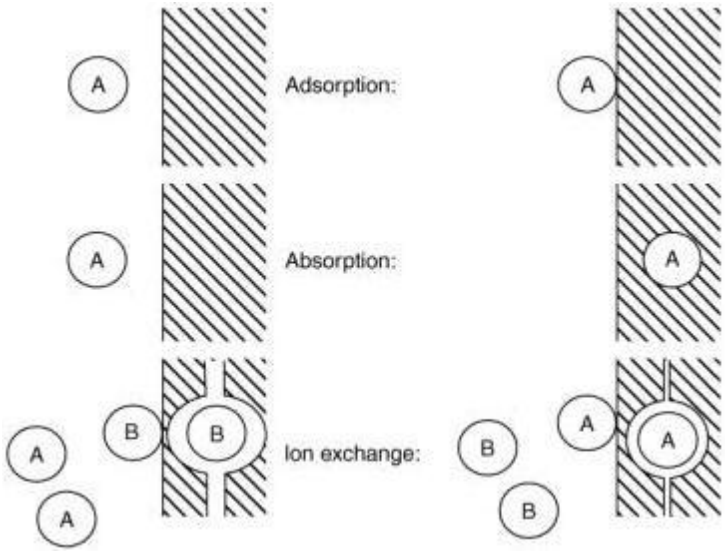

Figure 1.3: Representation of three sorption processes (Appelo and Postma, 2005)

A restricting factor in the decomposition of de-icing chemicals is the supply of oxygen and in 2011 a system for injecting air into the ground and groundwater along the western runway was tested. (OSL, 2011)

1.3. OSL Gardermoen: A case study

1.3.1. Airport at a glance:

Oslo Airport Gardermoen is Norway's biggest and busiest airport. The airport administration, Oslo lufthavn AS (OSL) has a policy directed towards ensuring a sustainable development of the airport and to maintain a balance between growth and efficiency with emphasis on social and environmental considerations.

1.3.2. Facts and figures about OSL:

OSl, (2011) gives some facts and figures about OSL which are shown in table 1.4

Table 1.4: Facts and figures about Gardemoen airport, Oslo

Runway lengths	2,950 and 3,600 metres
Air traffic capacity	65 aircraft movements per hour
Terminal building	148,000 square metres
Passenger capacity	OSL can handle a total of 8,000 arriving and departing passengers per hour
Annual passenger capacity	approximately 23 million
Airport area	13 square kilometres
Total areas for business development	2.7 square kilometres
Car parking capacity	16,363 car parking spaces, with 7,646 of these in multi-storey car parks
Other facts	In full operation from 8 October 1998 19.1 million passengers in 2010 212,311 aircraft departures/arrivals in 2010

1.3.3. Location:

The Gardemoen Delta is located at 40 kilometers to the north of Oslo. The new international airport for Oslo has been constructed over this Gardemoen aquifer which is the largest aquifer in Norway. This ice contact Delta was developed in the marine and mud sediments of Fjord basins. The origin of this delta dates back to the Pleistocene Period associated with the deglaciation period of Scandinavia almost 9500 years ago (Tuttle et al, .1997).

1.3.4. Hydrogeological foundation:

The map belows shows the quaternary geology of the area exposing the formations dominated by silty glacio marine deposits of sand and gravel. Furthermore the delta has two parts which are Trandum delta and the Li delta having an area of 79 km^2 and 58km^2, respectively. There are further 3 subunits of this delta having top sub unit consisting of coarse fluvial deposits including sand and gravel, middle sub unit having fine sands, whereas the lower most sub unit comprises of fine material.(Tuttle et al, .1997).

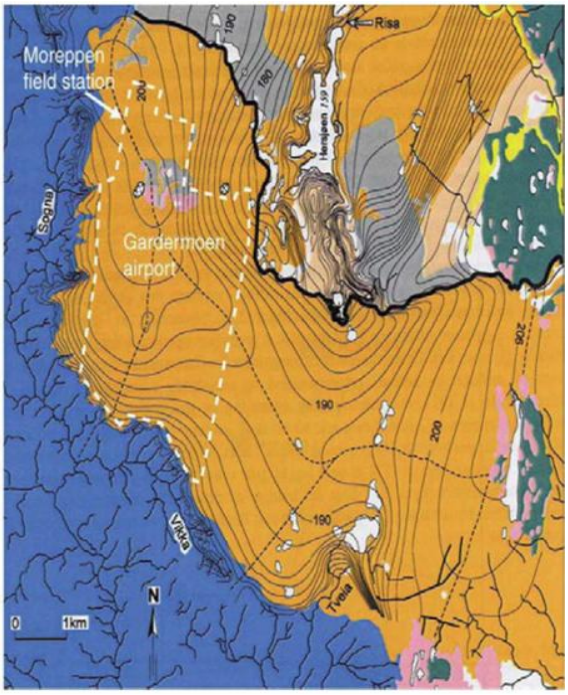

Figure 1.4: Quaternary Geological map showing the subsurface properties of Gardemoen delta (Tuttle 1997, modified by Aagaard and Breedveld 2008).

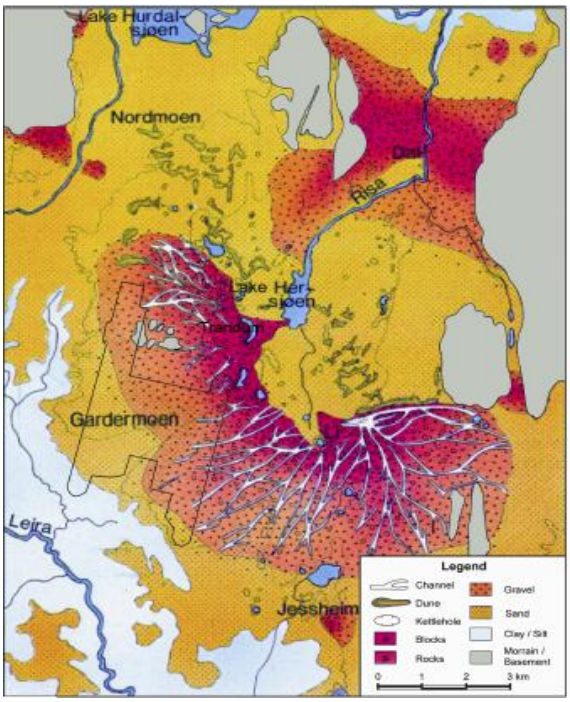

Figure 1.5: Map over sedimentary deposits location of surface water bodies near OSL.

The Gardemoen aquifer is the largest groundwater reserve of Norway having main recharge through rain water. The ground water table ranges between 1- 30 meters below the surface water and depends on the seasonal variations of precipitation. More than 70% of its water flows toward east feeding Lake Hersjoen and River Rissa and rest moves in western directions.

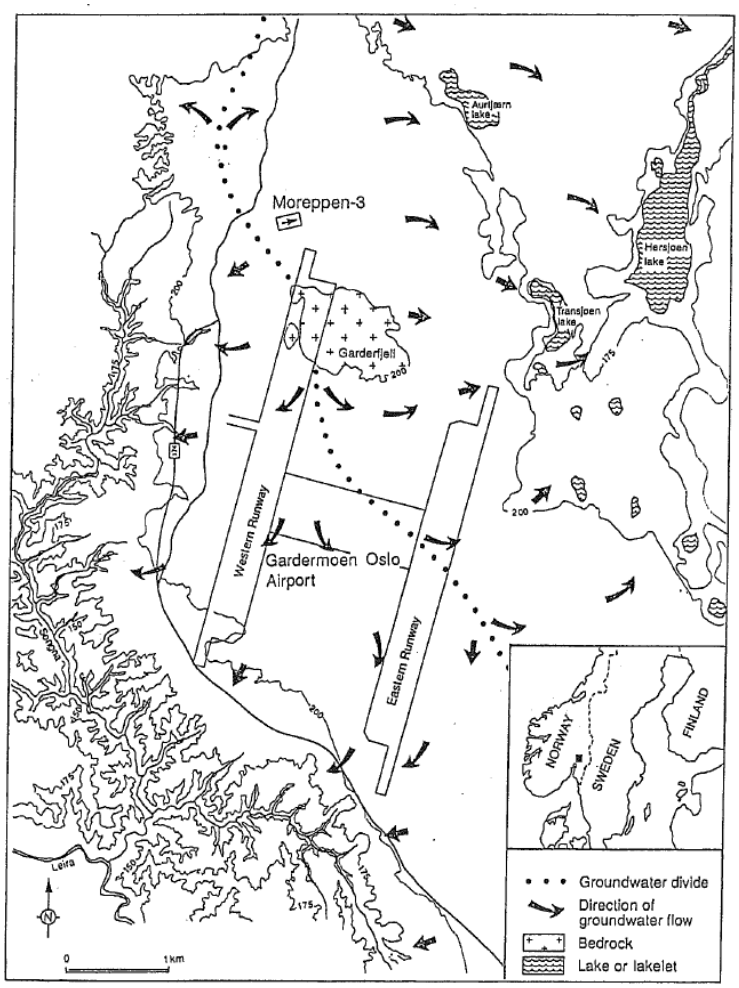

Figure 1.6: Ground water flow direction at Gardermoen (Aagaard P. and Breedveld G., 2008)

1.3.5. Climate:

The surface is covered by forest mainly spruce and open areas with pioneering vegetation, grass, bushes, young birch. The annual precipitation is approximately 800 mm and the evapotranspiration is about 400 mm. More than 50% of the groundwater recharge occurs during the spring season (French et al., 2001)

1.3.6. De-icing at OSL:

De-icing chemicals used during the winter season are potential pollutants for the groundwater underneath the main airport of Norway.

At the Oslo airport at Gardermoen, Norway, various de-icing chemicals are used. They include:

- **Kilfrost**, containing propylene glycol, also known as 1,2-propanediol,
- **Clearway 1**, containing potassium acetate (K-Acetate) and
- **Aviform L50,** containing potassium formate

These de-icing chemicals are used on airplanes and runways throughout the winter season (October–April). During mechanical removal of snow from the runways and by the airborne drift of chemicals from the air planes at take-off, the de-icing chemicals are mixed with snow. After winters with usually stable temperatures well above 0^{o}C, the chemicals infiltrate at the soil surface along the runways when the melting of snow begins around April. As the new airport is situated on the largest unconfined aquifer in Norway, it is important to ascertain that these chemicals do not contaminate the groundwater.

Glycol type 1, based on propylene glycol, has a specific weight of 1.045 kg/L, and a concentration of 80 %. This is a concentrate and needs to be diluted before use. There are "ready-to-use"-glycols in the market which are diluted 50-50 with water. Such mixtures are, however, not in use at OSL, because they have specialized vehicles that mix the Type 1 with water according to outside temperature to reduce the environmental load. Aviform L50, based on K-formate, has a specific weight of 1.35 kg/L and a concentration of K-formate of 50 % with water. Both fluids contain some additives, such as corrosion inhibitors.

1.3.7. Application of deicers at OSL:

The average consumption of deicers at OSL in the recent years is shown in table 1.5.

Table 1.5: Use of de-icing chemicals at OSL (Quantitative)

De-Icing Chemicals per Season					
Air Craft De-Icing					
	2005-6	2006-7	2007-8	2008-9	2009-10
Total Glycol Consumption (tonnes)	1748	1006	1027	1470	1481
Specific consumption of glycol (Kg/ Aircraft)	160	127	118	139	137
Collection rate of glycol (%)	80	81	85	79	80
Runway De-Icing					
Total Consumption of Runway De-Icing Chemicals (tonnes)	354	309	428	469	200
Environmental Load COD (tonnes KOF)	124	108	150	164	70

For the winter season 2009-2010, the consumption of de-icing chemicals was somewhat higher than the average for earlier years. However, the consumption of runway de-icing chemicals was found to be considerably lower than that of the previous season due to a cold and dry winter season with less precipitation. Eighty per cent of the aircraft de-icing chemicals used in this season were collected and put to use at external wastewater treatment plants.

The collection percentage for aircraft de-icing fluid was 76% during the 2010–2011 season.

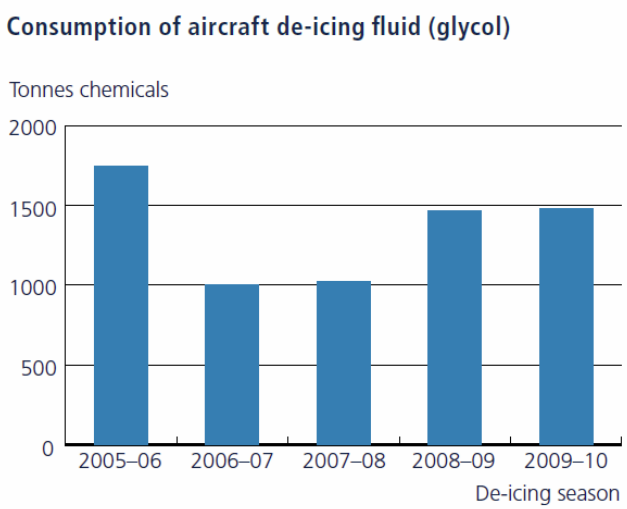

Figure 1.7: Consumption of propylene glycol at OSL (OSL 2010)

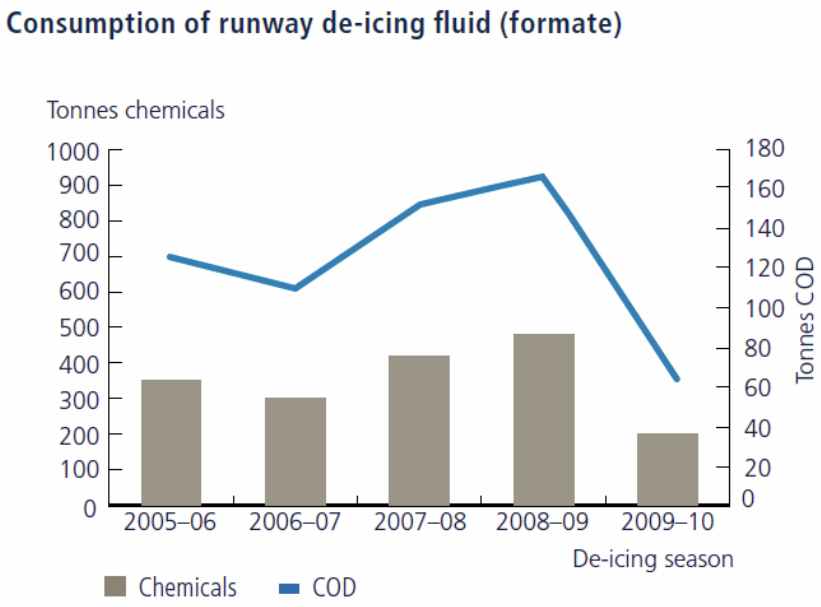

Figure 1.8: Consumption of formate at OSL (OSL 2010)

1.3.8. Policy regarding use of deicers:

In recent years, several important measures have been implemented, which reduce the emission of de-icing chemicals. This has provided improved control of the environmental impact on waterways and groundwater. Groundwater and river systems must not be degraded and air pollution should be minimized.

1.3.9. Observed environmental problems at OSL:

Runway de-icers are infiltrating in the unsaturated zone and depending on their fate and transport can be a potential pollutant to the groundwater. Field data from Oslo international airport at Gardermoen show that snow melting in springtime generates a relatively concentrated pulse of de-icers that infiltrate locally. Due to low soil temperature natural degradation processes are relatively slow. This might result in groundwater contamination and low-oxic/anaerobic conditions and potentially the reduction of iron and manganese minerals.

Oslo Airport extends over part of the Romerike aquifer and in the north, about half of the eastern runway overlies a potential future drinking water reservoir. In the northeast, the airport borders a nature preservation area and in the southwest it borders a landscape conservation area. The rivers Sogna and Vikka run through the ravines that characterize the landscape in the southwest. Surface water is generally processed locally at the airport. In the event of large run-offs, especially during snowmelts, there will be some influx of surface water from the western runway into the river Sogna. Along the western runway and the railway line, the natural water table has been lowered to protect the infrastructure. The groundwater that is pumped out is released into the Sogna river or re-infiltrated into the groundwater reservoir. Wastewater and some of the collected de-icing chemicals (glycol and formate) are processed at the Gardermoen treatment plant. Collected surface water with high glycol concentrations is delivered to other treatment plants as a carbon source for purification processes. The remainder of the de-icing chemicals degrades locally in the ground and along the runway systems.

Another area of focus is the evaluation of long-term effects of de-icing chemicals that are applied on runways and taxiways. In December 2010 the Norwegian ministry of Transport and Communications granted OSL permission to expand the terminal building. The project will increase the capacity of the airport to 28 million passengers per year. This will possibly results in increased air traffic and a consequent increase in the use of deicing chemicals. However, OSL emphasizes environmentally sustainable solutions for this development project, both during construction and in the subsequent operation of the new terminal areas.

At Oslo international airport, a total number of around 300 wells have been installed for monitoring, injection and remediation purposes. Some wells are individually installed where as some wells are in groups.

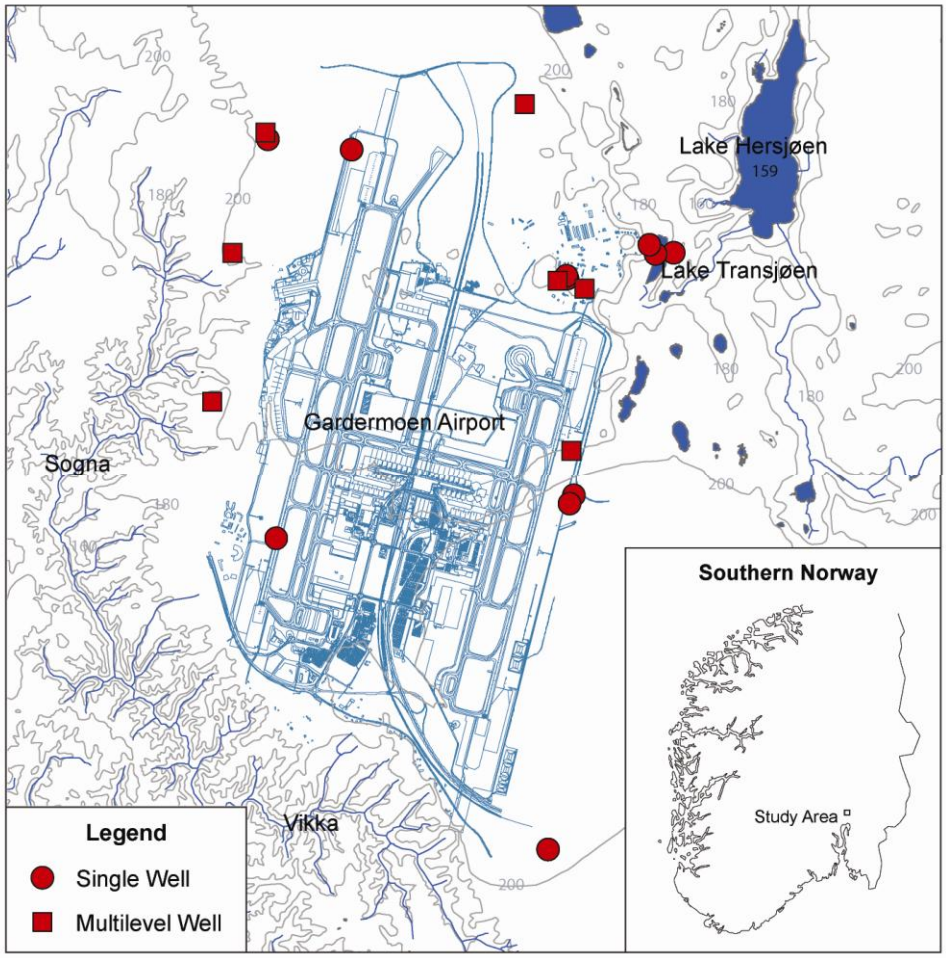

Figure 1.9: Monitoring wells inside and Outside OSL (Aagaard P. and Breedveld G., 2008)

1.4. Aim of the project

The main objective of this study is to determine the behaviour of de-icing chemicals in the unsaturated zone at OSL. How the de-icers interact with the soil, and the natural attenuation processes that determine transport and degradation. The focus will be on formate the main runway de-icer at Gardermoen.

Two different soil samples have been used in the experiments to do a general comparison of both soils, one from OSL which is exposed to formate over different de-icing seasons and the other from fluvial deposits of Glomma river which has never been exposed to de-icers.

One of the key issues during this study is to determine the changes in the chemical composition of the soil solution to determine the chemical, biological and physical processes occurring in the unsaturated zone which govern transport and degradation.

A proper understanding of the natural attenuation capacity of the soil is required to be able to prevent undesired reduction of the groundwater quality in a long-term perspective.

In this study, the transport and degradation of formate is studied in the laboratory on the bases of batch experiments and column experiments. The results of the experiments can improve the understanding of the natural attenuation processes in the unsaturated zone at Gardermoen.

Chapter 2: Background

2.1. Natural Infiltration Rates of different soil types:

The natural infiltration rate of different soil types determines the extent of permeability of infiltrating surface. Natural biodegradation capacity of soil is very much dependable on soil permeability and its natural infiltration tendency. The infiltration rates are determined by installing infiltrometers in the site (Bouwer, 2002).

Table 2.1: Infiltration rates of different soil types modified from (Bouwer ,1999) as cited in (Bouwer, 2002)

Soil Type	**Infiltration rate (m/day)**
clay soils	<0.1
loams	0.2
sandy loams	0.3
loamy sands	0.5
fine sands	1
medium sands	5
coarse sands	>10

2.2. Break through curves:

Break through curves give change in concentration while a solute is moving through a column. When a non reactive tracer is eluted through a column at a known concentration, the front will move with the average water flow velocity through the column. After intervals the curve gets the maximum concentration level.

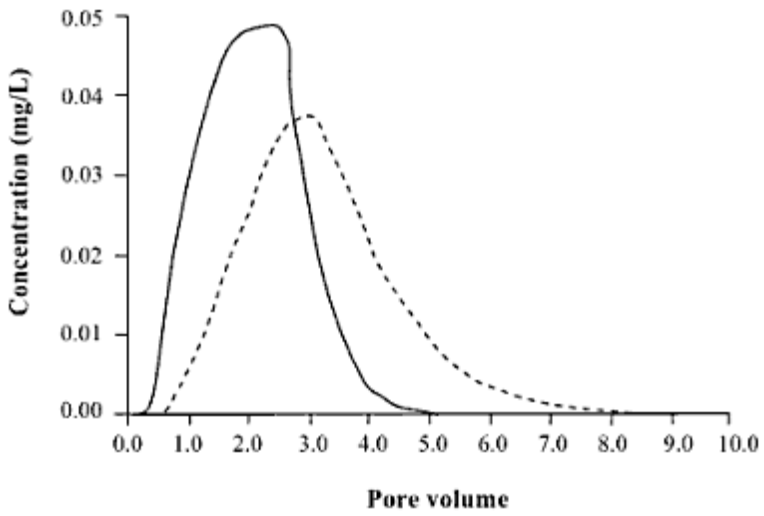

Figure 2.1: Example of break through curve. Dotted line shows retarded curve where as continuous line shows no retardation (Taylor and Aral, 2011)

2.3. Dispersivity:

Dispersivity within the column is equal to the representative grain diameter used in packing the column and when aquifer sediments are used in the column, the grain size is taken as d10, the diameter below which 10% of all the particles fall. The dispersivity is calculated by the equation suggested by (Perkins and Johnston, 1963)

$$\alpha_L = 3.5\ d_{10}$$

Where α_L is dispersivity in meters.3.5 is the shape factor which increases with smaller grain sizes. Usually in aquifer the dispersivity is much higher as compared to laboratory packed columns.

Diffusion Coefficient

Fick's First law is used to calculate the diffusion coefficient D from the given equation

$$F = -D\frac{\delta c}{\delta x}$$

Where

F = flux (mol/sec/m^2)

D=Diffusion coefficient (m^2/sec)

And

C= concentration (mol/m^3)

2.4. Longitudinal dispersion Coefficient:

The longitudinal dispersion coefficient or or the hydrodynamic dispersion coefficient (D_L) gives the rate of dispersion and is velocity dependent.

$$\mathbf{D_L = D_e + \alpha_L.v}$$

The diffusion Coefficient D_e becomes negligible if the v is higher than 1m/year.

Where

v = ground water velocity (m/s)

α_L =dispersivity (m)

2.5. Contaminant velocity and retardation factor:

The retardation factor shows how much the transport velocity of the contaminant differs compared to water traveling through the column.

$$v_c = \frac{v}{R}$$

where,

v_c = transport velocity of contaminant (m/s)

v = groundwater velocity (m/s)

R = retardatjon factor (-/-)

$$R = 1 + \frac{\rho_b}{n} \cdot K_d$$

where,

ρb = bulk density of soil (kg/l = ton/m3)

n = porosity (m3/m3)

K_d = distribution coefficient soil-water (l/kg)

2.6. Column load:

Column load is the concentration per unit area per day flowing through a column. It is given as

$$\textbf{Column load} = \frac{\boldsymbol{Conc.}\left(\frac{\boldsymbol{mg}}{\boldsymbol{lt}}\right).\boldsymbol{flow\ rate}\left(\frac{\boldsymbol{lt}}{\boldsymbol{day}}\right)}{\boldsymbol{CS\ area\ of\ column\ (m2)}}$$

2.7. Residence time:

Residence time is the time for which a concentration will stay in a column. It is calculated as

$$\boldsymbol{Residence\ time\ =\ pore\ water\ velocity/flow\ rate}$$

2.8. Pore water velocity:

Pore water velocity is defined as

$$\boldsymbol{Pore\ water\ velocity\ =\ (pore\ volume/\ CS\ area\ of\ Column)/\ porosity\ (n)}$$

2.9. The distribution Coefficient (Kd)

The distribution coefficient gives the distribution of a chemical between solid (q, mg/kg) and liquid phase (c, mg/l) represented as

$$\boldsymbol{Kd\ =\ q/c}$$

Chapter 3: Materials and methods

3.1. Sample description:

For our experimentation, we have considered two different kinds of soil samples, one which has been exposed to the deicers frequently over several years for various de-icing seasons and secondly a soil which has never been exposed to deicers. For the first purpose soil samples were taken along the western runway at OSL and for the later we used the fluvial soil samples from the Glomma River near the Elverum community which were already available at the sediment laboratory at the Department of Geosciences, University of Oslo. The samples were sieved and stored at room temperature i.e. 20^0C at their natural moisture level.

Soil samples from OSL:

The soil samples for our experiments have been taken from almost 70m distance from western runway, which is 3600m long. The well near sampling site is BR 29 which is further surrounded by two remediation wells. The ground water flow direction at this monitoring well is towards South west. The wells are having usual diameter of 2 inches and are surrounded by soil covered with grass. A team of 3 contaminant hydrogeologist is responsible for monitoring these wells twice a month.

Soil samples were taken by OSL staff after removing the upper grass cover and the samples were taken by digging with a spade down to 20-30 cm and preserved under normal refrigeration..

At OSL there are four de-icing platform at the two runways at OSL. The natural biodegradation capacity of the soil surrounding the runways has been decreasing yearly resulting from the application of deicers. Nutrient spreading methods (with nitrate) have been adopted to increase the natural biodegradation ability of the neighboring soil.

The red arrow mark shows the location of well BR 29 which is also our sampling location.

Figure 3.1: well locations at OSL

3.2. Experimentation:

A series of experiments were performed on both soil samples for physical and chemical analysis. These experiments involved soil characterization and batch experiments and column experiments.

3.2.1. Sieve analysis:

Standard mechanical sieving procedure is adopted to categorize the soil. The soils were air dried before sieving. Oven drying was a limiting factor for the microbial life. A standard set of sieves was used which included these grain sizes as demonstrated in the figure.

The soil from OSL was first sieved using sieve size of 3.35 mm to remove all the grass and dead organic remains from the sample. Then it was sieved according to the grain sizes of 2mm, 1mm,

0.5mm, 0.355mm, 0.250 mm, 0.180mm, 0.125mm, 0.090mm, 0.063mm and less than 0.063 mm this fraction was retained in the lower pan.

Samples of 1kg soil (air dried) were mechanically shaken for 15 minutes each in a specialized mechanical shaker with controllable time and vibration speed. Each pan constituents were weighed carefully using a digital balance. Based on this particle size distribution curves were constituted. Further the soil categorization curves were drawn to check the soil types.

3.2.2. Bulk density

The bulk density was measured by gravimetrical method. The inner volume of colums were measured and then they were filled with dry samples. The total difference in initial and final weight gave the mass of samples which was further used to calculate the bulk density

$$\text{Bulk density} = \frac{Mass\ of\ sample\ in\ the\ column}{Internal\ volume\ of\ column}$$

These tests were performed three times to check reproducibility.

3.2.3. Porosity:

The sample filled columns were pumped in with water with a known flow rate. The time was calculated until the water started dripping from the outlets of columns. With the known flow rates and time, total volume of water that entered the columns was measured and was considered as the saturated pore volume of the samples within the columns. Then the porosity was measured according to the following equation.

$$\text{Porosity} = \frac{Volume\ of\ water\ required\ for\ total\ saturation\ of\ samples}{Volume\ of\ soil\ sample\ within\ each\ colum} \times 100\%$$

Both columns were infiltrated water containing NaCl with known electrical conductivity and were checked for outlet conductivities and then retention curves were drawn to check the break through. These breakthrough curves gave us information about the retention times and porosities.

3.3. Batch Experiments:

Batch experiment was performed by mixing both soil samples with a solution containing K-formate (50mg/lt COD) and 0.001M $NaNO_3$.The samples were mixed on the ratio of 1:5 by mixing 20 grams of soil and 100 ml of solutions.3 samples from each soil were prepared for the procedure to ensure minimum chances of error. Then the samples were placed on a shaking table at a steady shaking rate for a period of one week. The containers were covered with cotton plugs and loose caps to ensure oxygen availability throughout the experiment. Samples for COD analysis were taken at day 7, 14 and 21 after the start of experiment, filtered and then frozen for later analysis. Syringe filters (0.45µm) were used for the purpose of filtration. Figure 3.2 shows the assembly for batch experiment.

Figure 3.2: Batch experiment assembly, The 3 bottles on LHS are filtered samples from OSL soil batch experiment. Yellow color is an indication of presence of Iron.

3.4. Column Studies:

Column experiments were performed to measure the natural biodegradation within the samples. The columns were operated at room temperature to ensure maximum biodegradation. The column assembly contained two different columns A and B of same specification containing the same samples. Both were connected to Teflon tubing at each end i.e. inlets and outlets. The inlets were connected to the inlet container via a peristaltic pump which could be operated at different flow rates giving a controlled flow. The inlet container comprised of a non reactive plastic container. The outlets were also connected with the outlet containers via Teflon plastic tubing. The outlet containers were covered with seals to avoid evaporation losses.

3.4.1. Column Specifications:

Each column used in the experiment was made up of stainless steel. A wire gauze filter was installed at both ends of column to avoid out flow of inner sediments.Both columns A and B were 50cm long and the internal diameter was 5cm.As the column were cylindrical in shape so volume of the columns were measured. The volume of each column was calculated as 982 cm^3.

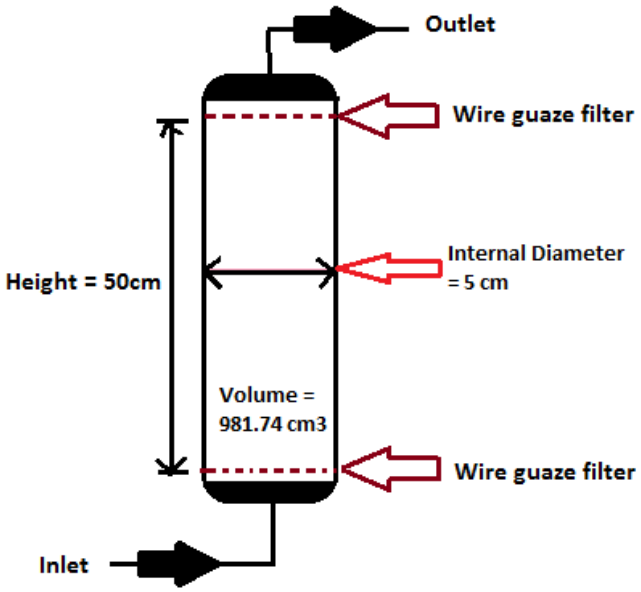

Figure 3.3: Column specifications

3.4.2 Soil Packing:

Soil packing was done by making a soil slurry and then pouring it into the columns. The slurry was made using de-ionized water. The masses of the dry soil samples were measured before pouring them into the column. The excess of water was drained from the lower end of columns under the influence of gravity and the mass of water and fine sediments were periodically calculated to ensure the accuracy of sediments being packed within the columns. The columns were tapped from the sides to ensure packing without any air bubbles. The purpose of slurry filling was to make sure that there are no air packets or air bubbles inside the columns.

Once filled, the upper wire gauze filters were applied and the columns were sealed tightly to avoid any possible leakage. Afterwards the columns were connected to the outlets and inlets via a peristaltic pump as shown in the figure 3.4.

Glass beads sized 1mm diameter were added on the top of the columns containing the samples from OSL below the wire gauze filter to avoid clogging of the filters by fine particles. These beads acted as a fine filter in upright position (figure 3.4).

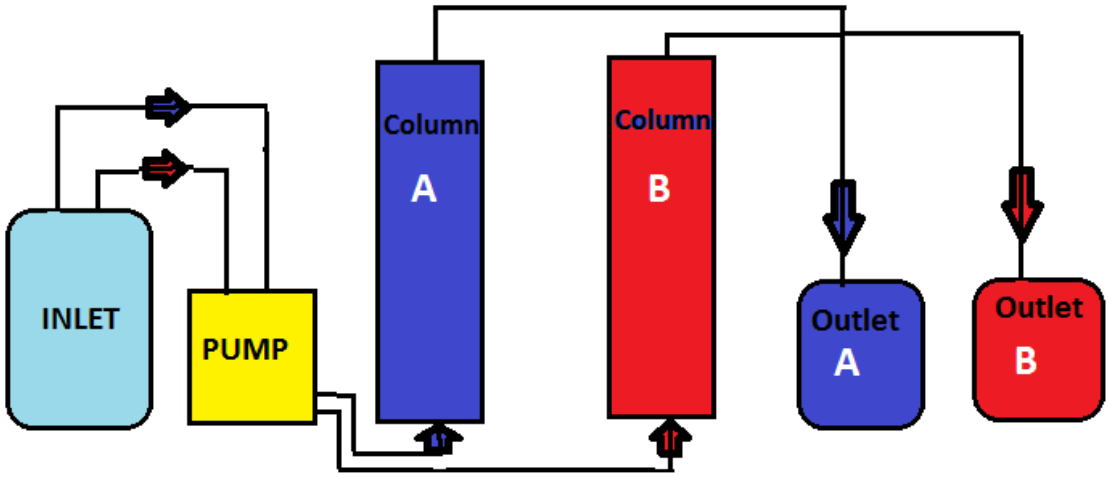

Figure 3.4: Assembly of Column Experiments

The columns were then left to run on de-ionized water for almost 48 hours so that maximum number of pore volumes should pass through the columns and make the columns completely air free.

3.4.3. Description of Column Experiments:

A series of six different column experiments were performed using the above mentioned setup. The description of experiments is given below

Experiment 1: Elution of NaCl Solution as Non reactive tracer through Elverum Soil Samples:

In this experiment both columns A and B were eluted with 0.01M NaCl solution at a controlled flow rate of 2.6 ml/minute and 2.7 ml/minute, respectively. The inlet solution had an EC of 1080 µS/cm. Both step up and step down experiments were performed in approximately 540 minutes and the inlet was changed to de-ionized water on getting stable concentrations in the column outlets.EC and outlet volumes were measured after every 10 minute intervals.

Experiment 2: Elution of K-Formate Solution through Elverum Soil Sample:

Before start of this experiment the columns were eluted with de-ionized water and after getting minimum EC through the outlets, the inlet was changed with K-formate Solution (50mg COD/lt) having an EC of 670 µS/cm. The step up and step down process was completed in 720 minutes and the inlet was switched to de-ionized water on getting stable concentrations from the outlets. The flow rates were same as that of experiment 1.Samples from outlets were preserved for COD analysis from selective intervals.

Experiment 3: Time Step Flow of K-Formate solution through Elverum Soil Samples

This experiment involves the elution of K-formate Solution (50mg COD/lt) from both columns at different flow rates over a period of 43 days. Flow rates were changed after every week time and the samples from inlet and both outlets were preserved for COD analysis before switching to new flow rate. The total volume eluted from each column was almost 83 litres. Different flow rates used in experiment 3 are given in table. The residence times and column loads are in appendix B.

Table 3.1: Flow rates in experiment number 3

Experiment 3	Flow rate (ml/minute)
Phase 1	0.113
Phase 2	0.538
Phase 3	1.159
Phase 4	1.718
Phase 5	2.430
Phase 6	3.125

Experiment 4: Elution of NaCl Solution as Non reactive tracer through OSL Soil Samples:

In this experiment both columns A and B were eluted with 0.01M NaCl solution at a controlled flow rate of 0.54 ml/minute .The inlet solution had an EC of 1080 µS/cm. Both step up and step down experiments were performed in approximately 49 hours and the inlet was changed to de-ionized water after getting stable outlet concentrations and then giving a gap of 36 hours on same flow rates..EC and outlet volumes were measured after every 10 minute intervals other than the 36 hour gap.

Experiment 5: Elution of K-Formate Solution through OSL Soil Samples:

Before start of this experiment the columns were eluted with de-ionized water and after getting minimum EC through the outlets, the inlet was changed with K-formate Solution (50mg COD/lt) having an EC of 670 µS/cm. The step up and step down process was completed in 60 hours and the inlet was switched to de-ionized water on getting stable concentrations from the outlets and the giving a gap of 34 hours. The flow rates were the same as that of experiment 4 .Samples from outlets were preserved for COD analysis from selective intervals.

Experiment 6: Time Step Flow of K-Formate solution through OSL Soil Samples

This experiment was performed using two different inlet solutions. For the first 7 days both columns were eluted with K-formate Solution (50mg COD/lt) having an EC of 670 µS/cm and in next four weeks the columns were eluted with K-formate Solution (50mg COD/lt) + 0.001M $NaNO_3$ Solution having EC of 862 µS/cm. $NaNO_3$ was added as extra nutrients for the microbial activity. Samples from inlet and outlets were measures for EC on daily basis and were preserved

for COD analysis. This experiment was performed with a controlled flow rate of 0.54 ml/minute from each column.

The Solution preparation standards are mentioned in appendix D.

3.5. Physical & chemical analysis:

A variety of chemical analysis was done both on the inlets and outlet solution. The soil samples were monitored for pH, Conductivity, TOC, COD,. The details are given in the following paragraphs.

3.5.1. pH:

pH of inlet and outlet solutions was measured using a standard digital laboratory pH meter. The pH of soil samples was also measured using t he standard procedure operated at the department of Geosciences, University of Oslo. The samples were preserved in reaction free glass containers for future reference in refrigeration. For Soil pH, the soil was mixed with de-ionized water (1:5) and also with 0.01M $CaCl_2.2H_2O$ (1:5).the mixtures were retained for 2 hours before pH readings.

Figure 3.5: Digital pH meter

3.5.2. Electronic conductivity measurement

The electronic conductivity of both inlet and outlet solutions was measured using electrical conductivity meter. As the conductivity is a temperature sensitive phenomenon, hence the measurements were done at 20-25 ^{o}C.

Figure 3.6: Digital Conductivity meter

3.5.3. Total Carbon measurement:

The soil samples were measures for total carbon contents by using standard procedures at department of geosciences, University of Oslo using the LECO (CR-412) carbon analyzer. First the samples were homogenized by crushing them in pestle and mortar. Then the samples were treated with HCl and were flushed with water to remove all the inorganic carbon, to measure the organic carbon present in the samples. The procedure works on the carbon dioxide measurement getting out from the reacting chamber of the sample. From the known values of total carbon and the total organic carbon, we can ultimately know the value of total inorganic carbon present in the sample.

The CR-412 carbon analyser is a non-despersive, infrared digitally-controlled instrument designed to measure the carbon content in a wide vaiety of materials such as coal, sediment and soil.

Analysis begins as a sample (0.3500g nominal) is placed in the combustion system of pure oxygen environment typically regulated at 1350◦C. All sample materials contained in the combustion boat go through an oxidative-reduction process that causes C-bearing compounds to break down and free the carbon. The carbon then oxidizes to form CO_2. From the combustion system the controlled gas flow through the infrared detection cell which measures the carbon dioxide gas present.

The instrument converts the values to a percentage/ppm value, using an equation present in software which takes into account the sample weight, calibration and the known moisture value.(US-EPA 2002)

Figure 3.7: LECO (CR-412) carbon analyzer

3.5.4. Chemical Oxygen Demand

The Chemical Oxygen Demand (COD) was performed using the USEPA reactor Digestion method. The HACH COD test vials were used for this purpose.2 ml of sample is added to the test vial and is heated in the heating block for 150 degree C up to 2 hours. This process is called as digestion. After digestion the vials are cooled down to room temperature and photometrical analyzed for absorbance at a wave length of 348nm (COD range 0-60 mg/lt) or 448 nm (COD range 0-150 mg/lt) depending on the test kit used. The calibration curves for both test kits are given in figures 3.10 and 3.11. The COD hating reactor and UV absorption spectrophotometer can be seen in figure 3.3 and 3.9, respectively.

Figure 3.8: COD reactor/Heating chamber,

Figure 3.9: UV mini- 1240 Absorbtion Spectrophotometer

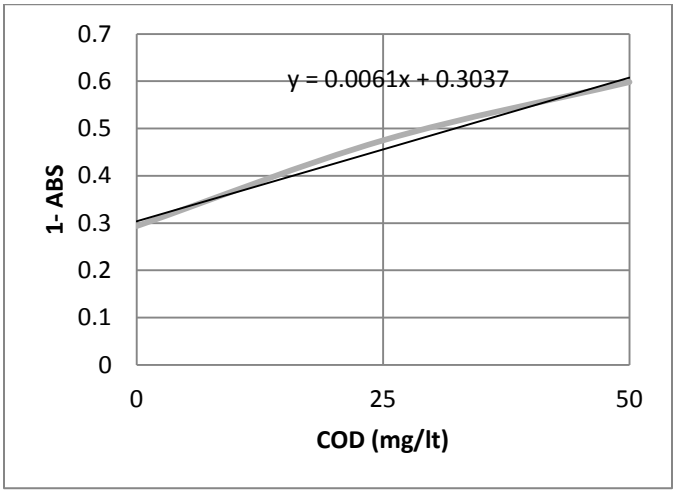

Figure 3.10: COD calibration high 448nm

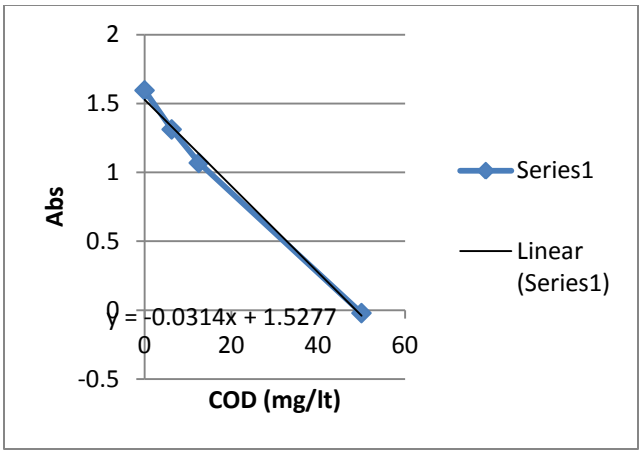

Figure 3.11: COD calibration Low 348nm

3.5.5. Iron and Manganese Analysis:

The samples from outlets of both columns and the water samples from batch experiment were analyzed for Fe and Mn using Atomic Absorption Spectrophotometer (AAS). The instrument used for this purpose was Varian Spectr AA300. This instrument works on the principle of light absorption. The elements present in the eluted sample are made to pass through a light energy of specific wavelength. The element in the sample enters the excited state from its ground energy state. This results in increased amount of absorbed light by the sample. Afterwards a quantitative determination of amount of analyte can be made by measuring the amount of light absorbed. AAS uses specific light sources and wavelength for different elements.

Figure 3.12: Atomic Absorption spectrophotometer, Varian Spectr AA300

Chapter 4 : Results and discussions

4.1. Soil Characterization:

4.1.1. Soil Parametres:

Table 4.1: Comparison of properties between Elverum and OSL soil samples

Parameter	Elverum Soil	OSL Soil
Bulk Density (g/cm^3)	1.47	1.72
Porosity %	35.7	33.5
Sand %	93.73	18.48
Silt + Clay %	6.16	81.52
Soil Class	Sand	Silt -Silt Loam
Soil pH (H_2O)	6.08	6.24
Soil pH (0.01 M $CaCl_2$)	5.98	5.53
Carbon (Inorganic) %	0.07 ± 1%	0.11 ± 1%
Carbon (organic)%	0.00 ± 1%	0.29 ± 1%
Carbon (Total)%	0.08 ± 1%	0.40 ± 1%
Hydraulic conductivity(m) (d10/d60)	0.0005	0.000375
$\alpha_L = 3.5\ d_{10}$	0.4375	0.1313

The results for carbon analysis can be found in appendix A-1.

4.1.2. Particle size distribution

The graphical results of particular size distribution and soil classification are given in figure 4.1 and figure 4.2, respectively. Tabulated results can be seen in appendix A-2.

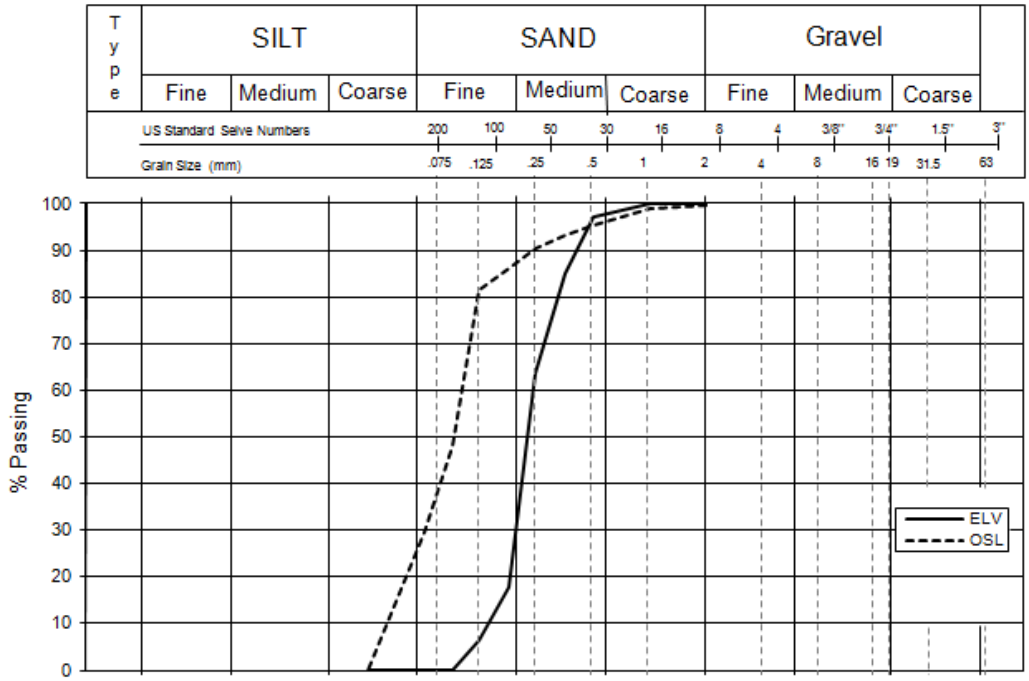

Figure 4.1: Particle size distribution of Elverum (ELV) and OSL soil samples

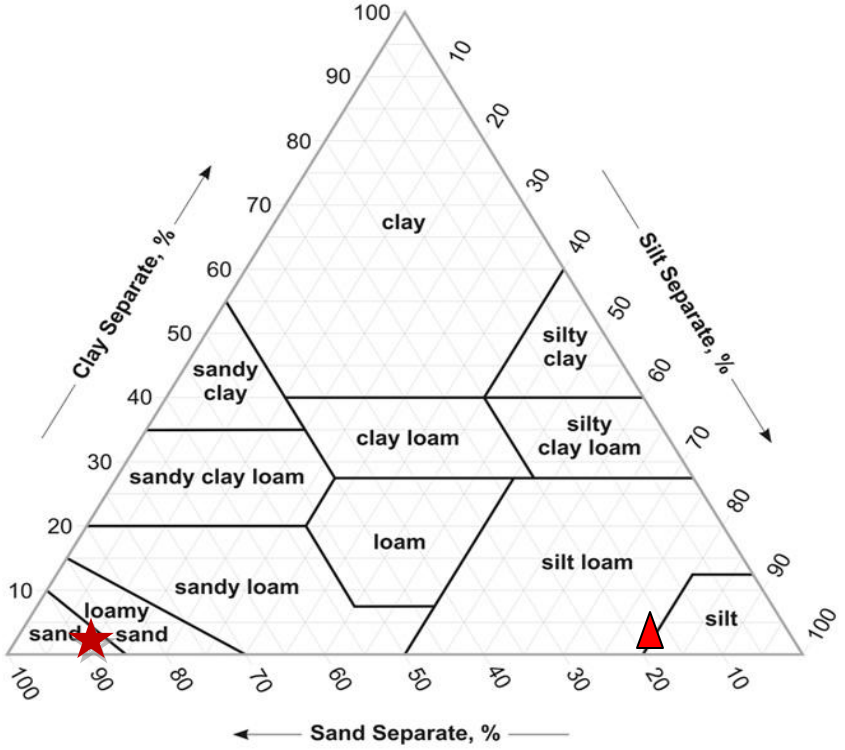

Figure 4.2: The soil classification triangle. Elverum Soil is represented by Star mark where as OSL soil is represented by triangle mark.

The soil from Elverum is sand where as the soil from OSL is silt to silt loam on the basis of classification. Elverum soil is a mixture of coarse , medium and fine sands OSL soil sample contains comparatively more fines. The clay fraction has not been measured separately and is included in the silt fraction. .

4.2. Batch Experiment:

The batch experiment results comprise of COD analysis results taken at 4 different intervals after the start of experiment. The measurement was taken at 3, 7, 14 and 21 days after the start of experiment. Fe and Mn analysis were performed on day 21. Figures 4.3 demonstrates the results from batch experiments.

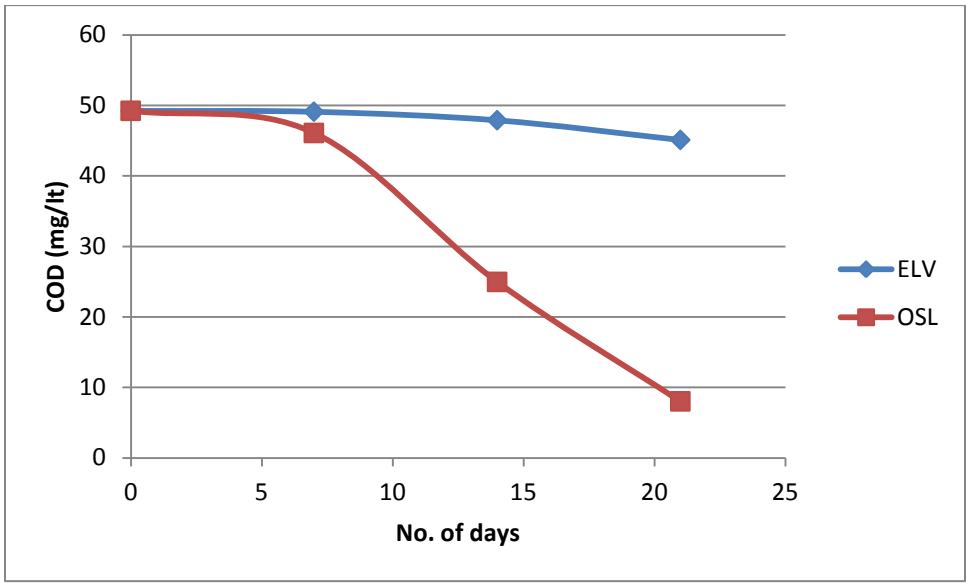

Figure 4.3: Results from batch experiment performed on Elverum and OSL soil samples

The results show almost 85% reduction of COD in OSL soil samples where as 12% reduction in COD in Elverum soil samples after 21 days of batch experiment.

4.3. Column Experiments

4.3.1. Column Experiments with Elverum Soil Samples

Experiment 1 : Elution of NaCl Solution as Non reactive tracer

The elution of NaCl solution as a non reactive tracer electrolyte shows almost the same behavior in both columns A and B (figure 4.4). The EC has been used as a parameter to measure the solute transport through the columns.

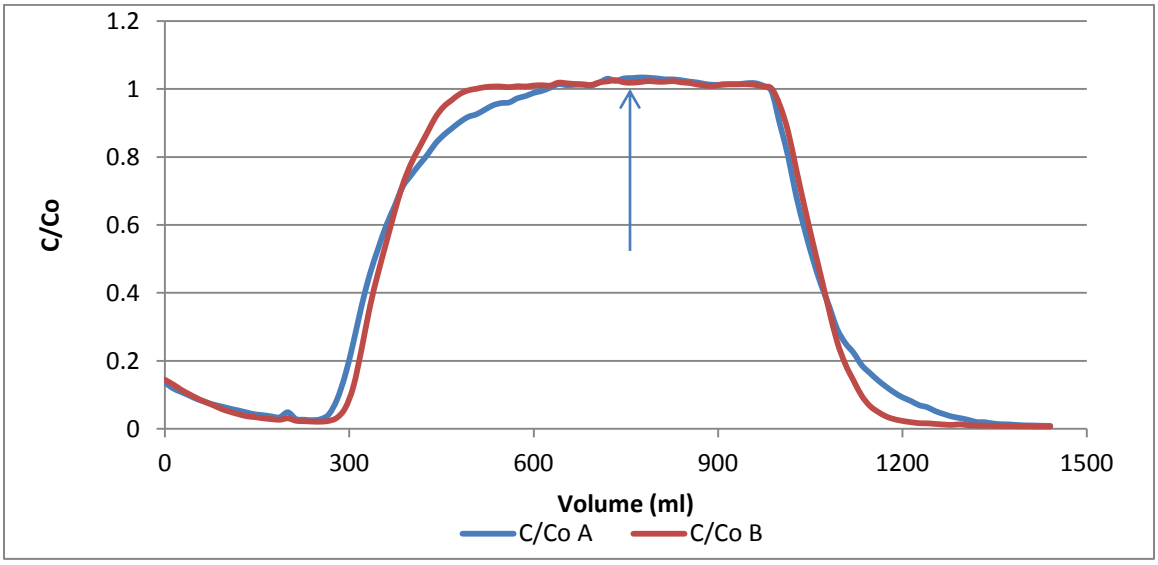

Figure 4.4: Change in Electronic conductivity during elution of NaCl Solution through Elverum soil. Arrow show change of inlet solution

The breakthrough curve (with increasing concentrations) and the outwash curve (with decreasing concentrations) show a similar pattern which means the NaCl solution behaves like a conservative tracer for water transport. The sample is composed of sand hence it has a high porosity. The uniformity of the curves shows proper packing of columns with no irregular peaks and fluctuations. The tabulated results can be found in appendix C-1.

Experiment 2: Elution of K-Formate solution

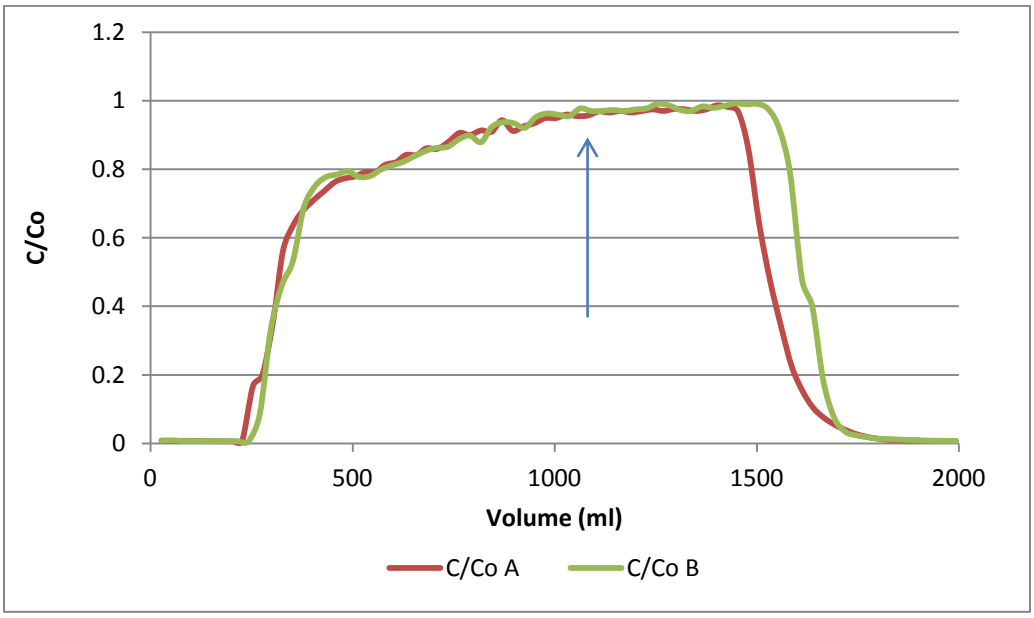

Figure 4.5: Change in Electronic conductivity during elution of K- Formate solution through Elverum soil. Arrow show change of inlet solution

The K-formate solution elution (figure 4.5) through the columns show almost the same behavior as that of NaCl solution. But during the breakthrough both columns show degradation which is clearly shown by the slowly rising concentration in both columns. This can be the result of the activity of microbes present in the soil. The outwash curve shows a rapid decrease with a more sharp front, showing that the elution of de-ionized water is rapid which might indicate formate removal by microbes . Sorption by TOC can also be a factor in retardation. The tabulated results can be found in appendix C-2.

Comparison of NaCl Solution and K-Formate Solution elution

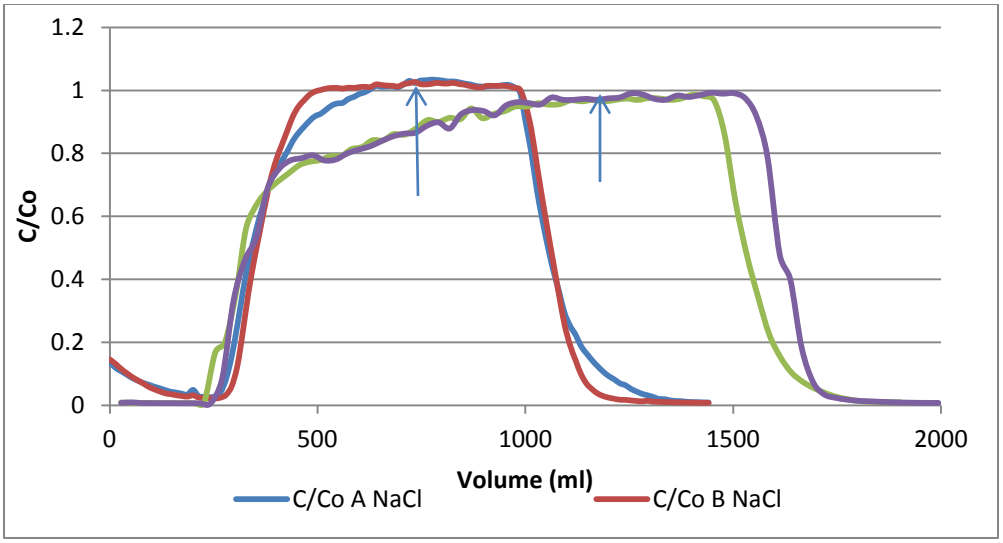

Figure 4.6: Comparison of change in Electronic conductivity during elution of NaCl Solution and K- formate solution in Elverum soil. Arrows show change of inlet solution

Comparing the chloride and formate curves (figure 4.6) can give us a clear picture of degradation in the columns containing Elverum soil. The formate solution requires more time to get its peak concentration as compared to the chloride solution. The slow ascend of formate in comparison to Cl^- solution indicates microbial degradation of formate. The retardation factor for K-formate is calculated to be 1.10. The tabulated results can be found in appendix C-4.

Chemical Oxygen Demand (COD) Analysis

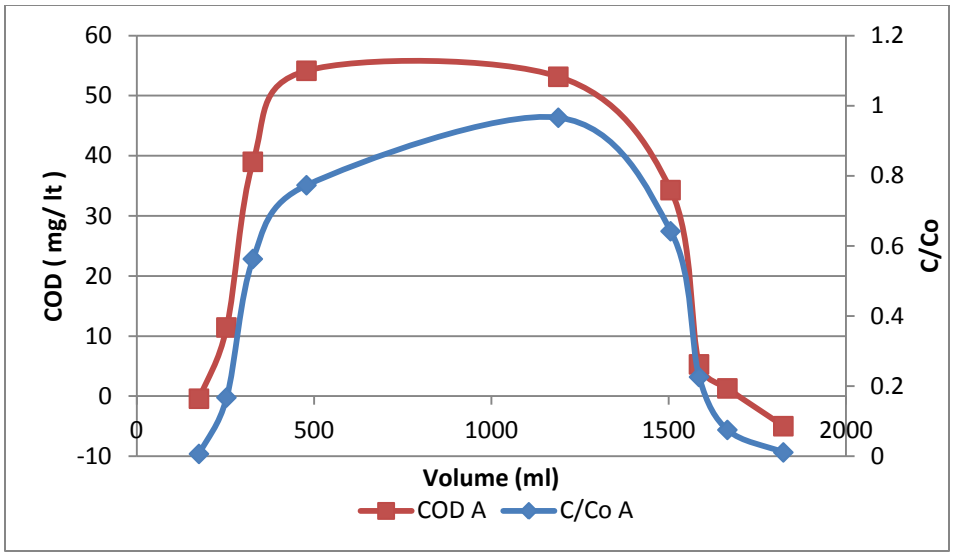

Figure 4.7: Change of COD in comparison to EC with respect to flow through column A for Elverum soil.

COD analysis were carried out on the in- and outlet samples of the formate experiment. Figure 4.7 shows relation of COD and EC in column A. The Results for COD analysis are given in appendix C-3. The results clearly indicate a good correlation between EC and COD measurements in the outlet from the column A. The difference between COD in and COD out loads are represented in appendix B-3. Appendix B-2 gives the reduction in COD loads.

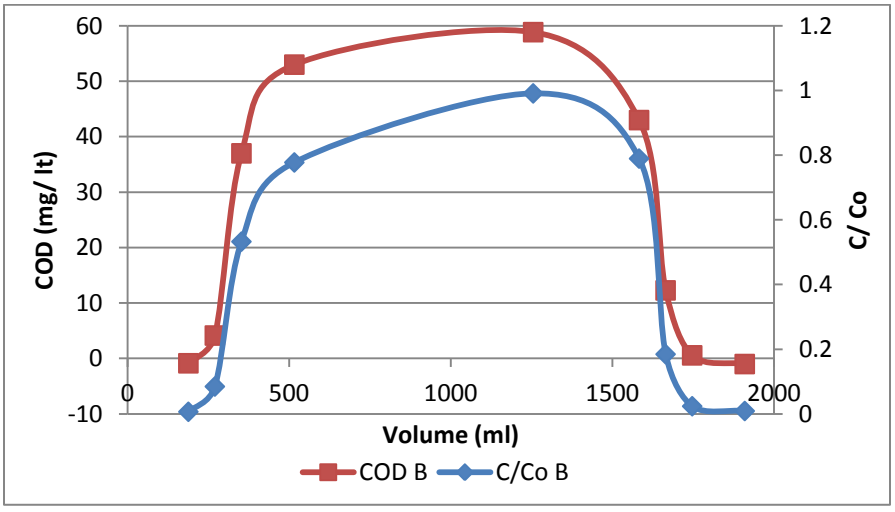

Figure 4.8: Change of COD in comparison to EC with respect to flow through column B for Elverum soil

Also in Column B (figure 4.8) a clear correlation between EC and COD is observed. COD results are used to determine solute transport and removal (appendix B).

Experiment 3: Time Step Flow of K-Formate solution

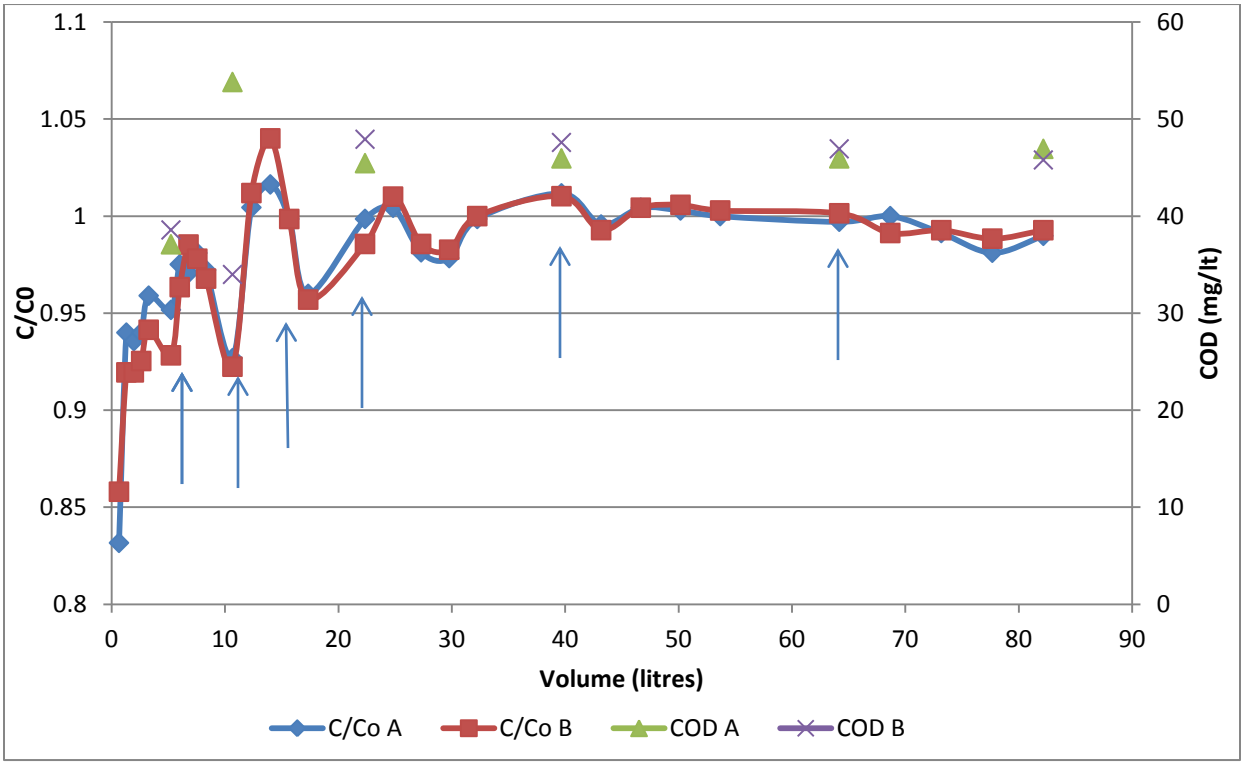

Figure 4.9: Time step experiment with different flow rates result of EC and COD measurements with respect to infiltration volume in Elverum soil. Arrows show change of flow rates.

This time step experiment explains the behavior of both columns with the elution of K-formate solution with a known COD value of 50mg/lt. At six different flow rates tend to change the residence time hence the columns behave in different ways. The overall trend is from lower flow rate and high residence times to high flow rates and low residence times; the column shows a stable descend in the concentrations resulting in a stable plateau.

There is no dramatic decrease in the EC but we can observe the fluctuations in the COD values which later become stable to a COD limit slightly below the COD in. At this stage we can interpret that we can see degradation in the columns as the COD decreases. But the reason why there is no further decrease in the COD values can be increased flow rates, resulting in increased loads of formate and a decreased residence time. This kind of constant low degradation rate by

the soil micro-organisms results in a higher outlet concentration. Another critical factor is the possibility of decrease of nutrients available for the microbial life. Figure 4.9 shows the graphical results for time step elution where as the complete results are tabulated in appendix C-5.

4.3.2. Column Experiments with OSL Soil Samples

Experiment 4: Elution of NaCl Solution as Non reactive tracer

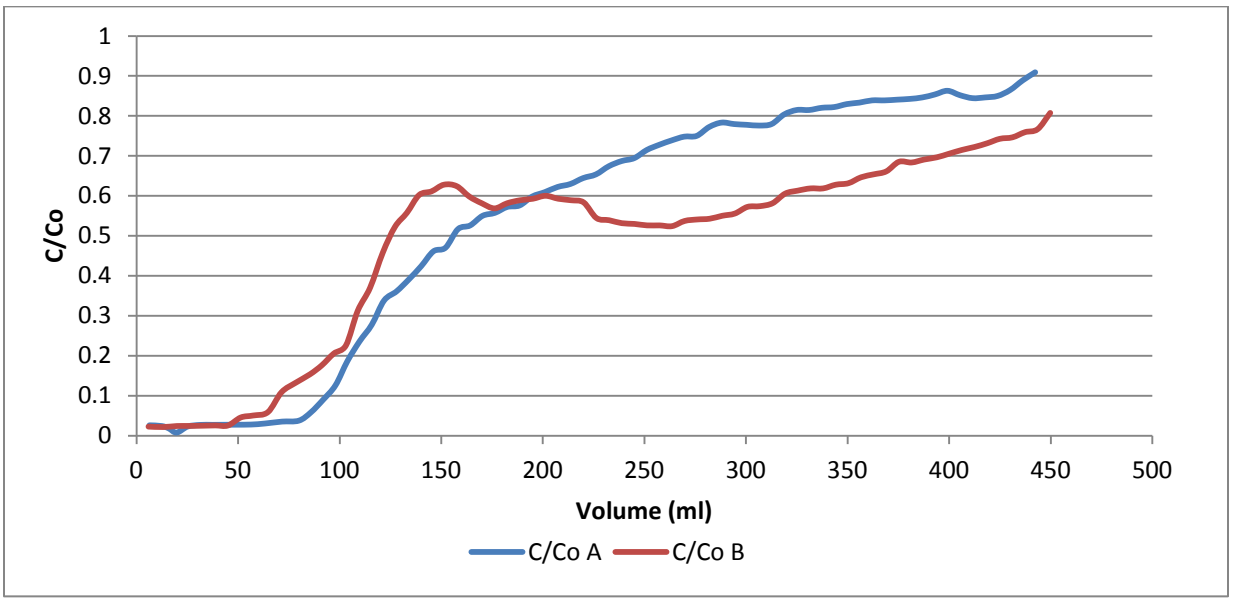

Figure 4.10: Change in Electronic conductivity during elution of NaCl solution for OSL soil

Both columns A and B show a slightly different behavior, but same trends in the breakthrough concentration with non reactive tracer electrolyte i.e NaCl solution (figure 4.10). The reason can be the presence of fine particles in the soil. OSL soil is silt to silty loam in classification resulting in low permeability and less solute velocities. The irregularity in the breakthrough near C/C_0=50 is because of loosing of fines out of the columns. Column A responds later but gives more response as compared to column B. We have tried to homogenize the soil before packing the columns but the delay observed for column A is possibly due to more biomass present in column A resulting in irregular flow through it. The presence of fine material like clays give an abrupt change in column flows because of swelling and hindering the solute transport. After fines have been washed out, both columns show a more similar behavior.

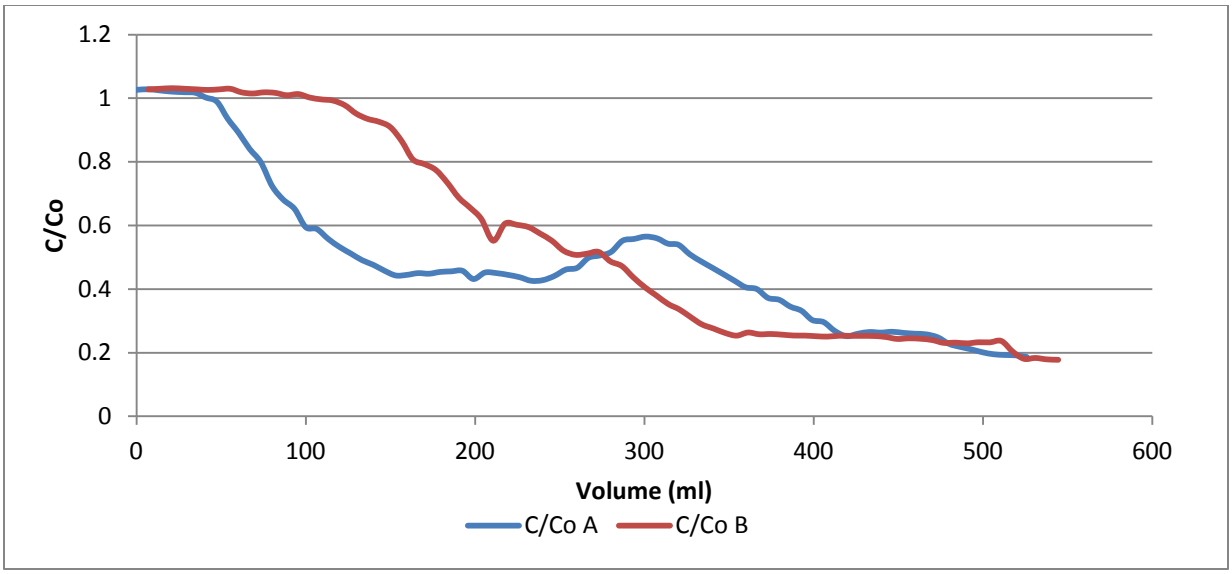

Figure 4.11: Change in Electronic conductivity during elution of NaCl Solution through column A and B

During out wash curve (figure 4.11) the observed changes in concentrations also marks some different behavior, but same trend in both columns. We know that the NaCl solution do not interact chemically with the soil and these fluctuations are because of possible air packets within the columns. Column A gives a fast response here and again shows a slightly different behavior at C/C_0=50 similar to that it had shown in break through curve.

To study the slow responses and irregularities in the flow patterns, a gap of 36 hours was given to the columns while they were kept on running on NaCl solution to get the peaks in flow patterns. The tabulated results can be found in appendix C-6.

Connecting the break through and out wash concentration curves (figure 4.12) after the above mentioned gap, we can clearly interpret that the step up and step down volumes are almost identical There is slight abruptions in the EC of outlet solutions but that can be because of variability in the flow rates because of possible air packets with in the columns and drainage of fines through the outlets.

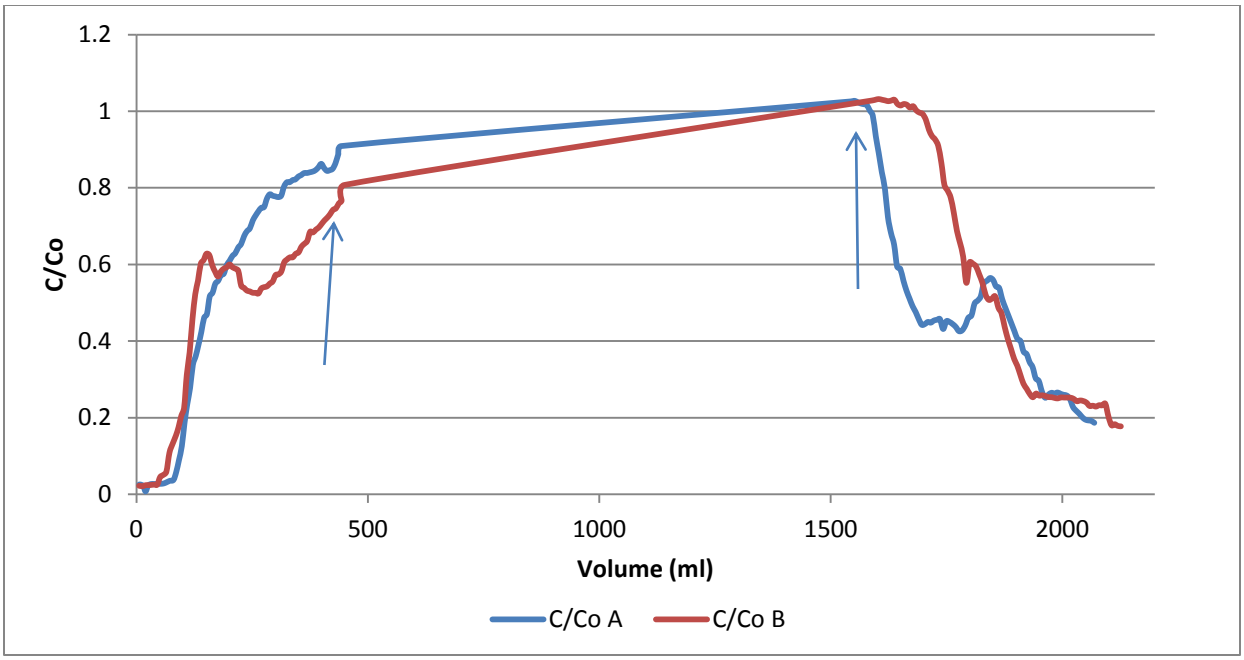

Figure 4.12: Change in Electronic conductivity during elution of NaCl for OSl soil.Arrows show gap of 36 hours in the experiment.

Experiment 5: Elution of K-Formate Solution through OSL Soil Sample:

Breakthrough curve:

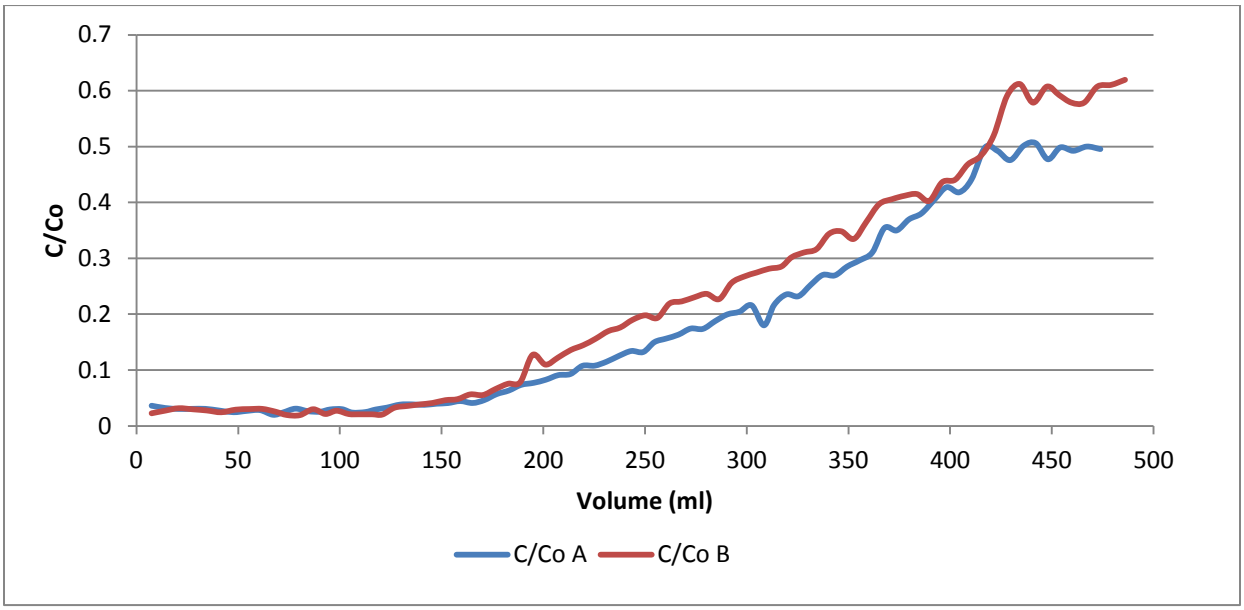

Figure 4.13: Change in Electronic conductivity during elution of K-Formate Solution OSL soil.

Both columns show similar pattern and behavior but with fluctuation because of drainage of fines from the column (figure 4.13). After the start of elution, the columns show no signs of change in the outlet concentrations for almost 150 ml of infiltration. While running on chloride in previous experiment, the concentrations started to change after 60 ml of elution. This means that the first initial low concentration of K-formate coming within the columns is degraded very rapidly. This slow response is clear indication of degradation.

Outwash curve:

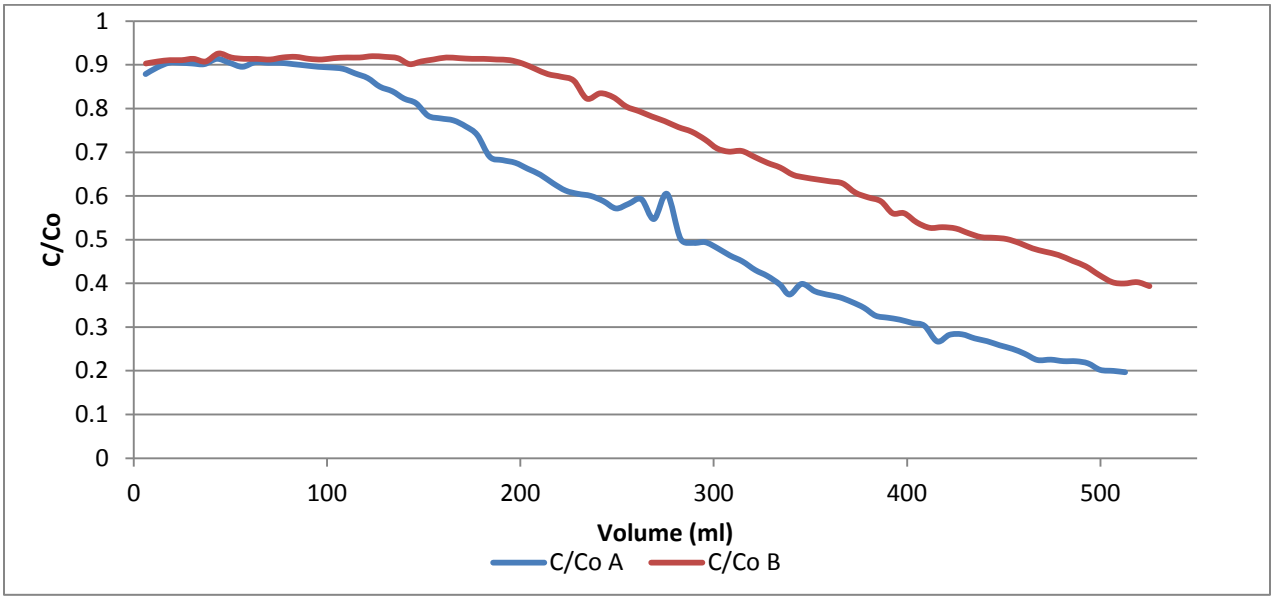

Figure 4.14: Change in Electronic conductivity during elution of Deionized water in OSL soil

Column B is showing slow response as compared to column A, Column A had shown more degradation and low solute travel velocity in break through curve. With the de-ionized water, we can see that the column A outlet solutions give response first as compared to column B. The column were packed making sure to remove all the trapped air bubbles, so these fluctuations in the concentration change are because of drainage of fines out of the columns or can be because of the change in rate of degradation ability of microbes at different intervals. Figure 4.14 represents the graphical results where as the tabulated results can be found in appendix C-7.

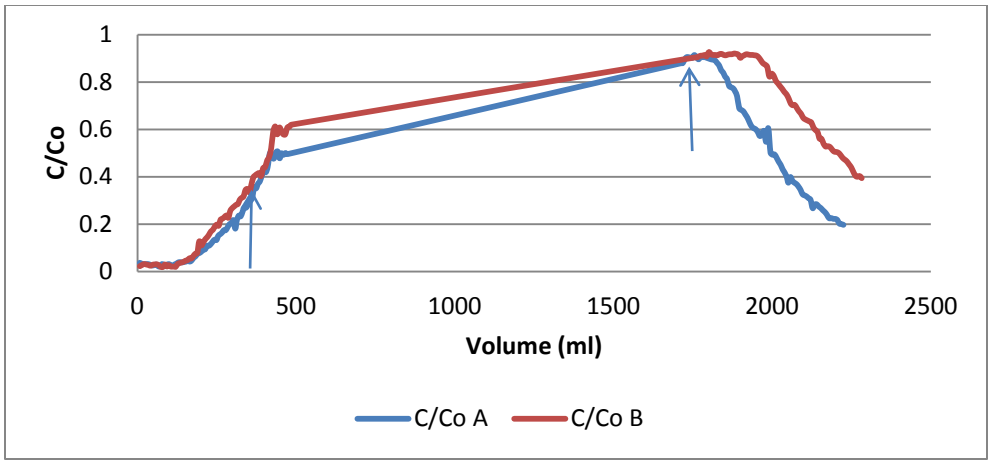

Figure 4.15: Change in Electronic conductivity during elution of K-Formate Solution for OSL soil. The arrows indicate gap of 34 hours in the experiment.

Combining both break through and out wash concentration curves (figure 4.15) with a gap of almost 34 hours shows similar initial behavior of both columns. Column B gets an initial rise and gets a higher peak in comparison to column B. During out wash we can see different behaviors as column B response is slower than that of column A. This is because of some variations in the flow rates between the two columns as column B has slightly higher flow rate than that of column B.

Comparison of NaCl Solution and K-Formate Solution elution:

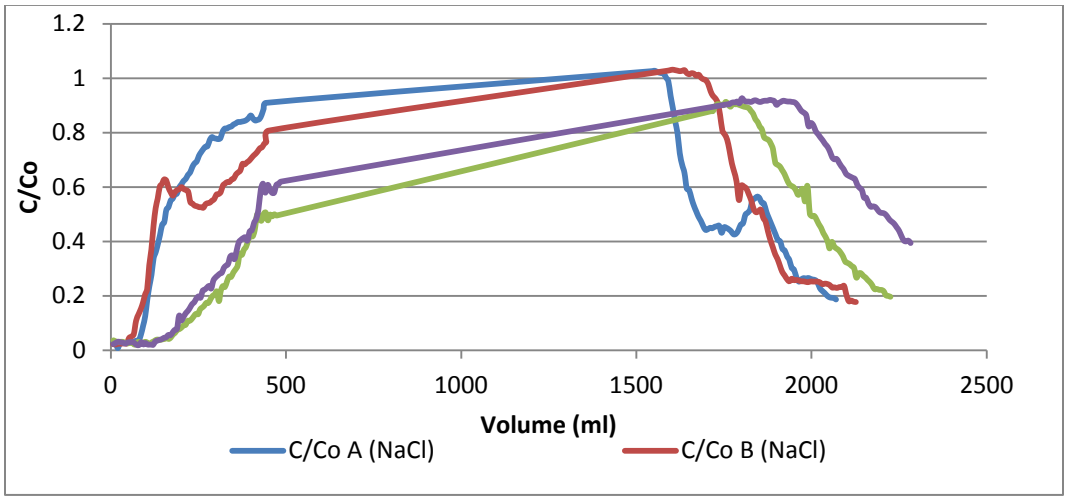

Figure 4.16: Comparison of change in Electronic conductivity during elution of NaCl Solution and K- formate solution for OSL soil

Comparing the chloride solution and formate solution elution through columns A and B (figure 4.16) shows clear degradation with the formate solution **.**We can assume the slow response of columns with formate is as a result of degradation resulting in retardation. The retardation here is calculated as 1.30 . The tabulated results can be found in appendix C-9.

Chemical Oxygen Demand (COD) Analysis:

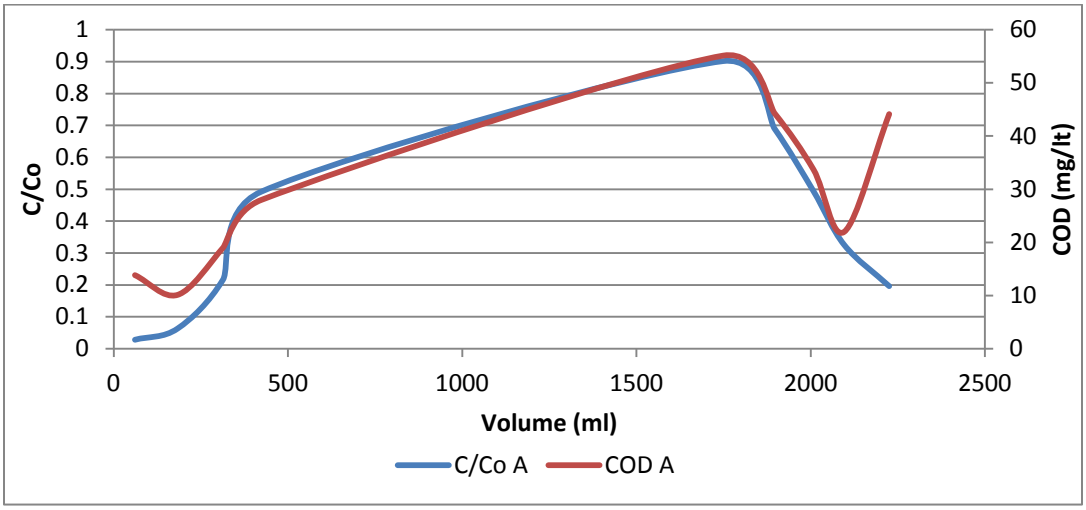

Figure 4.17: Change of COD in comparison to EC with respect to flow through column A, OSL soil

The change in concentration has a direct relationship with the change in COD throughout the flow in column A (figure 4.17) but the last part shows and unusual or abrupt increase in COD even with the decrease of concentration. This might be because of limiting ability of microbes to degrade formate due to lack of nutrients. The other reason is un-uniformity of flow because of trapped pockets of formate within the column that may come in the outlet at once or can be because of drainage of fines from the outlet.

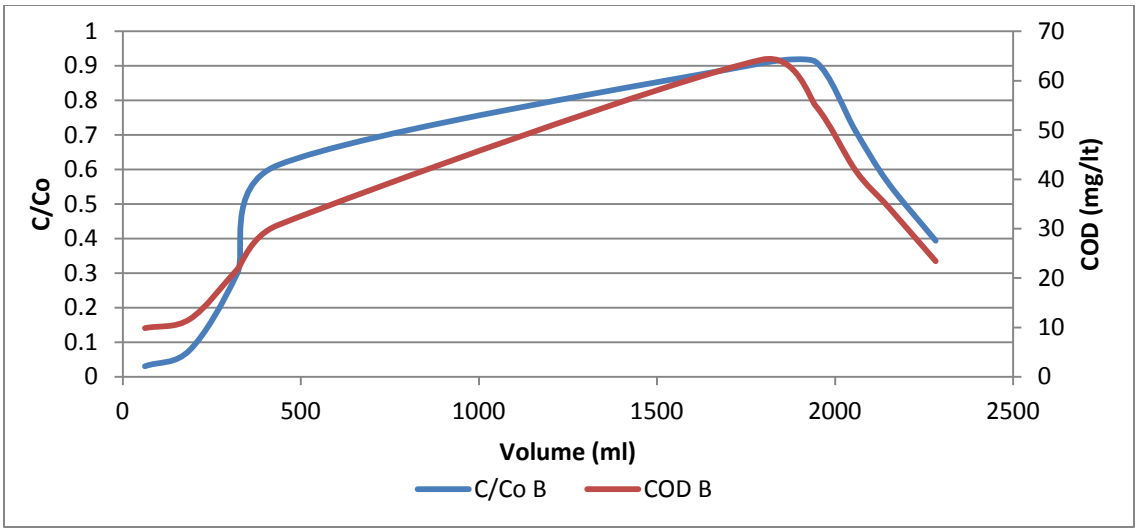

Figure 4.18: Change of COD in comparison to EC with respect to flow through column B, OSL soil.

Column B shows direct relationship between concentration and COD (figure 4.18). Unlike column A, the end part of COD curve has decreasing trend showing no unusual behavior. The tabulated results can be found in appendix C-8.

Experiment 6: Time Step Flow of K-Formate solution.

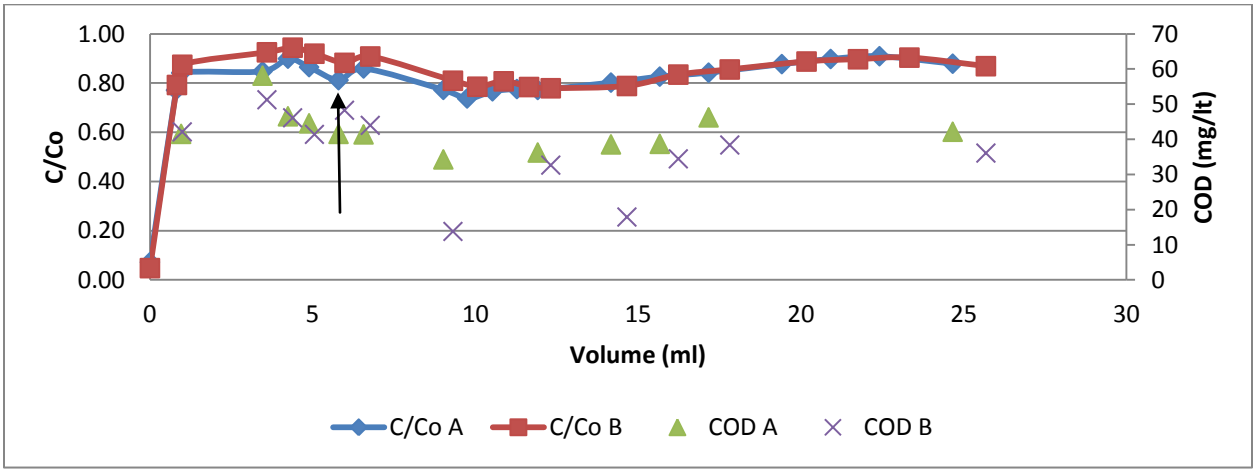

Figure 4.19: Time step experiment resulting in lowering EC and COD with respect to Volume for OSL soil. The arrow shows change of inlet solution.

The time step flow of K-formate through columns containing OSL soil starts from an initial concentration nearly zero as the columns were eluting de-ionized water. On switching to K-formate solution, the daily differences between concentrations (marked by EC) along with total eluted volume are demonstrated in figure 4.19. In the first stage of experiment, only K-formate solution was eluted and later $NaNO_3$ was added to provide the microbes with some nitrate as a source of nutrient and oxygen. The arrow shows change of inlet solution. The tabulated results can be found in appendix C-10.

Appendix B gives all the tabulated results of resident times, reduction in column load, COD reduction and EC removal for all the column experiments.

4.4. General Discussion:

Degradation rates, retardation factors, solute velocities and residence times through the unsaturated zone are important set of information to estimate whether the contaminant will reach down the aquifer or not. The more effective degradation results in less pollution in the aquifer.

Both batch tests and column experiments were performed to determine the natural degradation ability of the soil. The factor that influences the degradation in the soil is the microbial activity that depends upon the biomass present in the soil. Biomass is composed of living organism like soil micro-organisms and fungi, they can degrade organic contaminants. Generally, the more rich the soil is with biomass, the more will be the ability of soil to degrade the contaminants. Organic matter can be in the form of organic carbon resulting from the decay of living remains. Usually the upper layer of soil is rich in organic matter because of humic substances and continual decay processes. This organic matter helps in sorption of contaminants.

Certain limiting agents that can reduce the biodegradation are the deficiency of nutrients and oxygen limitation. Overall, in our set of experiments the Elverum soil samples are based on sand having low carbon content resulting in low sorption and the OSL soil has comparatively high carbon content resulting in high sorption.

The role of temperature is also an important aspect in the biodegradability but we have performed our experiments in laboratory facility with controlled room temperature facility,

giving emphasis to provide similar temperature conditions to both soil samples during experimentation.

The Elverum soil has never been exposed to deicers (Formate) in its life time but the OSL soil is continuously exposed to formate over the years. The OSL samples were taken in mid-June so that no traces of formate remained in the soil.

Higher infiltration rates decrease the residence time of contaminant resulting in reduce time for the microbes to degrade the contaminant. In the real situation, higher infiltration rates make the contaminant move faster through the most microbial active zone of soil which forms the upper 10 cm of the soil. Clogging is also a retarding factor which slows down the infiltration rates. In our procedures, we have taken the upper layers of soil, just after removing the grass layer and we made sure to minimize the clogging in the columns by controlling the flow rates and through proper packing and de-airing of columns.

Our main interest is to develop a comparison of natural degradation ability of both Elverum and OSL soils. The control in our experiments was NaCl solution as non reactive tracer electrolyte and then formate solution was eluted to check the change of concentrations in the outlet. The transport behavior of both formate and chloride solution have been discussed in the results along with the retardation with respect to change in residence time and flow rates.

In the column experiments performed on both soil samples, it is evident that formate solution has shown a similar pattern of displacement as that of non reactive tracer electrolyte. The general trend was initial fast movement of solute through the columns and later slow movements particularly with formate showing a degradation trend in the columns. This slowing down indicates adsorption. As discussed in the literature, adsorption is a main factor that slows down the solute movement in soil sediments and represents the natural tendency of sediments to attenuate some contaminant.

Similar results were demonstrated by French and co-workers (1999) for Acetate and Propylene glycol in the Gardermoen deposit using different experimental procedures. They calculated the retardation factor of acetate between 1.24 to 1.4. For chloride, the retardation factor was calculated as 1.15-1.25. Whereas propylene glycol had shown no retardation (retardation factor=1.01).

Retardation results from two processes taking place while a solute is moving through a column (in laboratory) or through some unsaturated zone (above an aquifer). These two processes involve degradation and adsorption. OSL soil has more attenuation ability as compared to Elverum soil.

The retardation factor for formate in Elverum soil and within OSL soil samples is given in table 4.2.

Table 4.2: Retardation factors

Experiemnt	**Sample**	**Solution**	**Rf**
1-2	Elverum	K-Formate	1.10
4-5	OSL	K-Formate	1.30

The sorption has a direct influence from the amount of TOC present in the sample. In our cases OSL soil has more TOC as compared to Elverum soil samples, and the results also prove more attenuation in the OSL samples because of more sorption. The TOC in OSL was 0.40% where as in Elverum soil TOC is nearly 0%. There are very less chances for a fluvial soil to have TOC as compared to some agricultural or forest soil. As the OSL soil had grass cover at the sampling location, hence this can possibly be a reason of accumulation of organic matter in the topsoil.

The sorption coefficient (Kd) for formate was calculated and is given in table 4.3

Table 4.3: Sorption coefficient (Kd)

Experiment	**Sample**	**Solution**	**Kd**
1-2	Elverum	K-Formate	0.024
4-5	OSL	K-Formate	0.05

High Kd values indicate higher sorption with in OSL soil as compared to Elverum soil.

Table 4.4: Contaminant Velocity

Experiment	**Sample**	**Solution**	**Vc (m/s)**
3 (II)	Elverum	K-Formate	$7.57*10^{-5}$
6 (I)	OSL	K-Formate	$6.75*10^{-5}$

Elverum soil has a high solute velocity which means that contaminant can be transported faster in this soil. The salute velocity of formate in OSL soil sample at laboratory flow rate indicates that formate can reach the aquifer (distance =6m) in 1.01 days. It is notable here that we have used higher flow rate in the laboratory columns which is almost 5 times higher than the natural infiltration rates of OSL.

The diffusion constant D has been calculated for formate elution in the columns by Ficks Law.

Table 4.5: Diffusion constants observed for chloride and formate in soil samples

Sample	**Solution**	**D (m^2/sec)**
Elverum	NaCl	$1.34*10^{-2}$
Elverum	K-Formate	$1.29*10^{-2}$
OSL	NaCl	$1.46*10^{-3}$
OSL	K-Formate	$1.38*10^{-3}$

Elverum soil samples have high diffusion coefficients, which indicate more faster transport of salute in the columns.

The Hydrodynamic dispersion Coefficient (longitudinal Dispersion Coefficient, D_L) for both soil samples is calculated by assuming the water velocity higher than 1m/year and considering the value of De as zero.

Table 4.6 : Longitudinal Dispersion Coefficient (D_L) for soil samples from Elverum and OSL in different column experiments

Experiment	**Sample**	**Solution**	**$D_L = \alpha_L . v$ (m)**
3(II) (Avg)	Elverum	K-Formate	$3.29* 10^{-5}$
6 (II) (Avg)	OSL	K-Formate + $NaNO_3$	$8.8*10^{-6}$

Presence of more fine particles in the OSL is a reason of low D_L for OSL samples. More D_L results in more rapid transport of salute.

Consideration was also given to change in color of stored outlet solutions under good oxygen supply to check whether Fe and Mn present in the outlet solutions use oxygen to make their colored oxides. Most of the Fe and Mn present in the aquifer result from such an anaerobic biodegradation in the unsaturated zone. As suggested by (Appelo and Postma, 1996) presence of Fe and Mn is an indication of redox conditions in the aquifer. As we are supplying the columns with a degradable chemical substance (formate), in the absence of oxygen or nitrate, Fe and Mn will act as electron acceptors. Reduction of Fe3+ to Fe2+ and Mn 4+ to Mn 2+ results in a high solubility of iron and manganese minerals and they can get dissolved in water easily. With the outlets of Experiment 6(II), we observes rusty yellow color which is an indication of presence of iron. In the reduced form Fe gets oxidized first in comparison to Mn and makes colored oxides in the outlets which have good supply of oxygen. The results for Fe and Mn Analysis for column outlets are given in table4.7, and for batch experiments in table 4.8. These results have an accuracy up to ± 0.10.

Table 4.7: Results for Iron (Fe) and Manganese (Mn) analysis (column outlets)

Experiment	**Inlet Solution**	**Column**	**Fe (mg/lt)**	**Mn (mg/lt)**
6 (II)	K-Formate + $NaNO_3$	A	1.30	0.05
6 (II)	K-Formate + $NaNO_3$	B	1.31	0.04

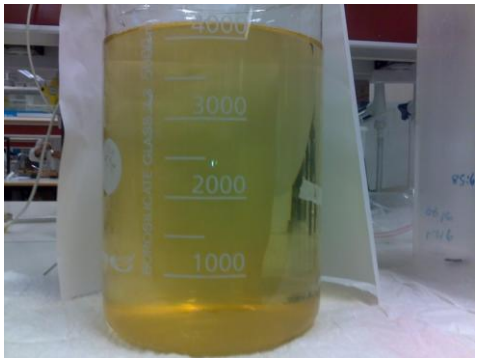

Figure 4.20: Outlet from column B at the end of experiment 6 (II), Yellow colur indicates presence of Iron

Table 4.8: Results for Iron (Fe) and Manganese (Mn) analysis (batch Experiment)

duration	**Inlet Solution**	**Sample**	**Fe (mg/lt)**	**Mn (mg/lt)**
21 days	K-Formate + $NaNO_3$	OSL	6.05	0.12
21 days	K-Formate + $NaNO_3$	ELV	0.13	0.01

After 21 days, the batch experiments show 85% COD reduction in OSL soil samples where as 12% COD reduction in Elverum soil samples. Presence of Fe and Mn can be taken as indicators of degradation activity during the experiment.

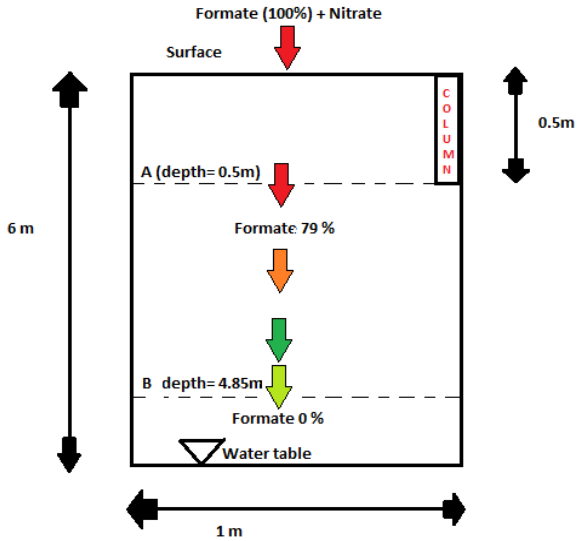

Figure 4.21: Depth model

We have tried to develop a model which will use our laboratory analysis and experimentation results into the real field environment of OSL. From the data of our columns and known column load, we can interpret how much natural attenuation can be expected for a deicer application on an area of $1m^2$ with a groundwater table at a depth of 6m.

It shows that without the addition of nitrate, OSL soil can degrade 91% of formate before it reaches the aquifer. On addition of nitrate, 100% reduction can be achieved at the depth of 4.85 m. This model is demonstrated in figure 4.21

Chapter 5: Conclusion

OSL soil has a porosity of 33.5% and a TOC 0.29 % where as the porosity and TOC of Elverum soil samples is 35.7% and 0.1% respectively. The retardation factors for formate relative to the inactive tracers (NaCl) have been calculated from the break through curves generated after column elution and is 1.10 for Elverum soil samples where as 1.3 for the OSL soil samples. The sorption coefficient Kd for formate is calculated as 0.05 in OSL soil samples where as 0.024 for Elverum soil samples. Formate travels slower in OSL columns (V_c= $6.75*10^{-3}$m/s) as compared to Elverum samples (V_c= $7.57*10^{-3}$m/s). The Diffusion constants for formate in OSL samples is calculated as $1.38*10^{-3}m^2/s$ where as in Elverum soil samples it is calculated as $1.29*10^{-2}m^2/s$. The longitudinal dispersion coefficient D_L is calculated as $3.29* 10^{-3}$ m for Elverum where as $8.8* 10^{-6}$ m for OSL. The presence of Fe (1.30 ppm) and Mn (0.05 ppm) in the OSL column outlets indicates the redox processes during elution of formate along with nitrate. Column load reduction for formate elution was calculated as 7.5% for Elverum soil samples where as 15.5 % for OSL soil samples. It is concluded that addition of nitrate can increase the attenuation of formate with a factor of nearly 5%. COD reduction rate in OSL soil samples is 36% (after addition of nitrate) and 11% (without nitrate). Lower flow rates have given higher concentration removal (7.5%) as compared to concentration removal during high flow rates (0.2-5%). Overall OSL soil has more attenuation capacity as compared to Elverum soil. This attenuation capacity can be increased by addition of nutrients (nitrate) and aeration of aquifer.

The batch experiments show 85 % reduction in the COD load for OSL soil samples after 21 days from the start of experiment where as for Elverum soil samples; this reduction factor is 12%. Fe and Mn concentrations in OSL batch samples were 6.05 ppm and 0.12 ppm, respectively. This is an evidence that Fe and Mn may be aa good indicator for degradation in unsaturated zone.

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Appendix A: Soil Characteristics

Table A-1 Carbon measurement

Sample	TC%	TOC%	TIC%
Elverum 1	-0.06	-0.06	0.00
Elverum 2	0.10	-0.08	0.18
Elverum 3	-0.03	-0.06	0.03
OSL 1	0.40	0.31	0.09
OSL 2	0.39	0.28	0.11
OSL 3	0.42	0.29	0.13

Table A-2 : Sieve analysis

Sieve size (mm)	ELV		OSL	
	Retained %	Passing %	Retained %	Passing %
2	0	100	0.22	99.78
1	0.02	99.98	1.11	98.89
0.5	2.80	97.20	4.57	95.43
0.355	14.81	85.19	6.80	93.20
0.25	36.16	63.84	9.44	90.56
0.18	82.09	17.91	13.79	86.21
0.125	93.73	6.27	18.49	81.51
0.09	99.89	0.11	52.03	47.97
0.063	99.98	0.02	70.49	29.51
0.0315	100	0	100	0

Appendix B: Removals

Table B-1: EC removal in experiment 3

Exp. No 3	EC (out) µS/cm	Flow (ml) /Hour Q	ECin µS/cm	ECout*Q	ECin*Q	EC removed (ECin*Q)-(ECout*Q)	EC Removed /day µS/cm
1 A	650	6.78	683	4407	4630.7	223.7	9.3
1 B	634	6.78	683	4298.5	4630.7	332.2	13.8
2 A	633	32.28	683	20433.2	22047.2	1614	67.2
2 B	630	32.28	683	20336.4	22047.2	1710.8	71.2
3 A	696	69.54	674	48399.8	46869.9	-1529.8	-63.7
3 B	687	69.54	674	47773.9	46869.9	-904.0	-37.6
4 A	690	103.08	682	71125.2	70300.5	-824.6	-34.3
4 B	689	103.08	682	71022.1	70300.5	-721.5	-30.0
5 A	687	145.8	689	100164.6	100456.2	291.6	12.1
5 B	690	145.8	689	100602	100456.2	-145.8	-6.0
6 A	682	187.5	689	127875	129187.5	1312.5	54.6
6 B	684	187.5	689	128250	129187.5	937.5	39.0

Table B-2: Reduction in Column Load

Exp.	Col.	Time	Inlet	EC_e (µS/cm)	EC/EC_e (Out) (Max)	Pore Vol. (ml)	Pore Water Velocity (max) (cm/min)	Column Load (g/cm^2/hour)	Flow rate ml/min	Residence Time (hours)	Reduction %
1	A	540 min	0.01M NaCl	1080	1.01	338	0.48	4.05	2.6	0.18	-1
1	B	540 min	0.01M NaCl	1080	1.01	351	0.50	4.21	2.7	0.19	-1
2	A	720 min	K-formate (50mg COD/lt)	670	0.98	338	0.48	4.05	2.6	0.18	2
2	B	720 min	K-formate (50mg COD/lt)	670	0.99	351	0.50	4.21	2.7	0.19	1
3 (I)	A	7 days	K-formate (50mg COD/lt)	670	0.95	338	0.48	0.176	0.113	4.24	5
3 (I)	B	7 days	K-formate (50mg COD/lt)	670	0.92	351	0.50	0.176	0.113	4.42	8
3 (II)	A	7 days	K-formate (50mg COD/lt)	670	0.92	338	0.48	0.83	0.538	0.89	7.3
3 (II)	B	7 days	K-formate (50mg COD/lt)	670	0.92	351	0.50	0.83	0.538	0.92	7.6
3 (III)	A	7 days	K-formate (50mg COD/lt)	670	0.99	338	0.48	1.80	1.159	0.41	2.4
3 (III)	B	7 days	K-formate (50mg COD/lt)	670	0.98	351	0.50	1.80	1.159	0.43	1.43
3 (IV)	A	7 days	K-formate (50mg COD/lt)	670	1.01	338	0.48	2.68	1.718	0.28	-1
3 (IV)	B	7 days	K-formate (50mg COD/lt)	670	1.01	351	0.50	2.68	1.718	0.29	-1
3 (V)	A	7 days	K-formate (50mg COD/lt)	670	0.99	338	0.48	3.79	2.43	0.20	0.29
3 (V)	B	7 days	K-formate (50mg COD/lt)	670	1.0	351	0.50	3.79	2.43	0.21	-0.15
3 (VI)	A	7 days	K-formate (50mg COD/lt)	670	0.98	338	0.48	4.875	3.125	0.15	1.02
3 (VI)	B	7 days	K-formate (50mg COD/lt)	670	0.99	351	0.50	4.875	3.125	0.16	0.73

Exp.	Col.	Time	Inlet	EC_o (µS/cm)	EC/EC_o (Out) (max)	Pore Volume (lt)	Pore Water Velocity (max) (cm/min)	Column Load ($g/cm^2/day$)	Flow rate ml/min	Residence Time (hours)	Reduction %
4	A	49 hours	0.01M NaCl	1080	1.02	341	0.52	0.842	0.54	0.96	-2
4	B	49 hours	0.01M NaCl	1080	1.03	347	0.527	0.842	0.54	0.97	-3
5	A	60 hours	K-formate (50mg COD/lt)	670	0.90	341	0.52	0.842	0.54	0.96	12
5	B	60 hours	K-formate (50mg COD/lt)	670	0.91	347	0.527	0.842	0.54	0.97	10
6 (I)	A	7 days	K-formate (50mg COD/lt)	670	0.89	341	0.52	0.842	0.54	0.96	18.8
6 (I)	B	7 days	K-formate (50mg COD/lt)	670	0.94	347	0.527	0.842	0.54	0.97	11.8
6 (II)	A	Day 7 – day 32	K-formate (50mg COD/lt) + 0.001M $NaNO_3$	862	0.77	341	0.52	0.8420 K-formate +0.841 $NaNO_3$	0.54	0.96	22.8
6 (II)	B	Day 7-day 32	K-formate (50mg COD/lt) + 0.001M $NaNO_3$	862	0.80	347	0.527	0.8420 K-formate +0.841 $NaNO_3$	0.54	0.97	19.03

Table B-3: Reduction in COD load

Experiment	Coloumn	Inlet	Flow Rate		Time	COD		CS. Area of Col	COD Load			Removal
						In	Out		In	Out	Diff	
			ml/min	lt/ day	days	mg/lt	mg/lt	m2	mg/lt/m2/day			%
2	A	K-formate (50mg COD/lt)	2.6	3.7	0.375	55.1	54.1	0.001963	105141.2	103234.4	1906.8	1.8
	B		2.7	3.9	0.375	55.1	53.0		109185.1	104947.6	4237.5	3.9
3 I	A		0.1	0.2	7	45.6	37.1		3779.0	3074.6	704.4	18.6
	B		0.1	0.2	7	45.6	38.6		3779.0	3198.9	580.1	15.4
3 II	A		0.5	0.8	7	53.3	53.8		21030.2	21227.4	-197.3	-0.9
	B		0.5	0.8	7	53.3	34.0		21030.2	13415.1	7615.0	36.2
3 III	A		1.2	1.7	7	43.2	45.5		36719.8	38674.8	-1955.0	-5.3
	B		1.2	1.7	7	43.2	47.9		36719.8	40714.8	-3995.0	-10.9
3 IV	A		1.7	2.5	7	49.7	46.0		62619.9	57958.1	4661.8	7.4
	B		1.7	2.5	7	49.7	47.6		62619.9	59974.0	2645.9	4.2
3 V	A		2.4	3.5	7	53.3	46.0		94987.5	81978.0	13009.5	13.7
	B		2.4	3.5	7	53.3	46.9		94987.5	83581.9	11405.6	12.0
3 VI	A		3.1	4.5	7	50.5	46.9		115737.6	107487.0	8250.6	7.1
	B		3.1	4.5	7	50.5	45.8		115737.6	104966.0	10771.6	9.3
5	A		0.5	0.8	2.5	58.1	28.0		23026.2	11088.8	11937.4	51.8
	B		0.5	0.8	2.5	58.1	30.7		23026.2	12163.7	10862.5	47.2
6 I	A		0.5	0.8	7	50.4	41.6		19971.2	16463.5	3507.7	17.6
	B		0.5	0.8	7	50.4	48.3		19971.2	19122.5	848.6	4.2
6 II	A	K-formate (50mg COD/lt) + 0.001M NaNO3	0.5	0.8	25	53.9	36.3		21329.0	14375.8	6953.1	32.6
	B		0.5	0.8	25	53.9	32.7		21329.0	12950.1	8378.8	39.3

Appendix C: Tabulated Experimental Results

Table C-1: Experiment 1 , NaCl Solution Break through and wash out curve from Elverum Soil samples , Inlet EC =1060 µS/cm

Time (mins)	Accumulative Volume (ml)	EC A (µS/cm)	EC B (µS/cm)	C/Co A	C/Co B
0	0.0	144	153.5	0.14	0.14
5	13.3	126	139	0.12	0.13
10	26.7	114.5	122.3	0.11	0.12
15	40.0	103.2	108.1	0.10	0.10
20	53.4	91.6	94.8	0.09	0.09
25	66.7	83	83.5	0.08	0.08
30	80.0	74.8	72.9	0.07	0.07
35	93.4	68.9	61.5	0.07	0.06
40	106.7	62.2	53.2	0.06	0.05
45	120.1	56.8	46	0.05	0.04
50	133.4	50.5	39.6	0.05	0.04
55	146.7	45	36.8	0.04	0.03
60	160.1	42.2	33.3	0.04	0.03
65	173.4	38.4	30.6	0.04	0.03
70	186.8	35.5	28.7	0.03	0.03
75	200.1	51.4	33.2	0.05	0.03
80	213.4	30.2	25.5	0.03	0.02
85	226.8	28.2	24.3	0.03	0.02
90	240.1	26.7	23.1	0.03	0.02
95	253.5	29.8	22.7	0.03	0.02
100	266.8	44.9	25.3	0.04	0.02
105	280.2	91.1	35.3	0.09	0.03
110	293.5	167.8	65.3	0.16	0.06
115	306.8	270	132.8	0.25	0.13
120	320.2	384	250	0.36	0.24
125	333.5	482	380	0.45	0.36
130	346.9	561	486	0.53	0.46
135	360.2	634	581	0.60	0.55
140	373.5	693	675	0.65	0.64
145	386.9	755	761	0.71	0.72
150	400.2	790	826	0.75	0.78
155	413.6	823	876	0.78	0.83

160	426.9	854	924	0.81	0.87
165	440.2	890	972	0.84	0.92
170	453.6	916	1005	0.86	0.95
175	466.9	937	1026	0.88	0.97
180	480.3	957	1045	0.90	0.99
185	493.6	973	1056	0.92	1.00
190	506.9	981	1061	0.93	1.00
195	520.3	995	1066	0.94	1.01
200	533.6	1009	1068	0.95	1.01
205	547.0	1016	1068	0.96	1.01
210	560.3	1018	1066	0.96	1.01
215	573.6	1031	1069	0.97	1.01
220	587.0	1038	1068	0.98	1.01
225	600.3	1048	1071	0.99	1.01
230	613.7	1054	1072	0.99	1.01
235	627.0	1064	1071	1.00	1.01
240	640.3	1075	1080	1.01	1.02
245	653.7	1072	1078	1.01	1.02
250	667.0	1073	1076	1.01	1.02
255	680.4	1073	1075	1.01	1.01
260	693.7	1071	1073	1.01	1.01
265	707.0	1080	1081	1.02	1.02
270	720.4	1092	1084	1.03	1.02
275	733.7	1085	1088	1.02	1.03
280	747.1	1093	1081	1.03	1.02
285	760.4	1094	1080	1.03	1.02
290	773.7	1096	1082	1.03	1.02
295	787.1	1095	1085	1.03	1.02
300	800.4	1093	1083	1.03	1.02
305	813.8	1090	1083	1.03	1.02
310	827.1	1090	1085	1.03	1.02
315	840.5	1087	1081	1.03	1.02
320	853.8	1083	1079	1.02	1.02
325	867.1	1080	1074	1.02	1.01
330	880.5	1075	1071	1.01	1.01
335	893.8	1073	1070	1.01	1.01
340	907.2	1073	1075	1.01	1.01
345	920.5	1075	1075	1.01	1.01
350	933.8	1075	1075	1.01	1.01
355	947.2	1078	1075	1.02	1.01
360	960.5	1078	1073	1.02	1.01

365	973.9	1070	1068	1.01	1.01
370	987.2	1053	1062	0.99	1.00
375	1000.5	952	1010	0.90	0.95
380	1013.9	852	929	0.80	0.88
385	1027.2	727	811	0.69	0.77
390	1040.6	625	695	0.59	0.66
395	1053.9	533	585	0.50	0.55
400	1067.2	452	478	0.43	0.45
405	1080.6	384	372	0.36	0.35
410	1093.9	311	272	0.29	0.26
415	1107.3	267	202	0.25	0.19
420	1120.6	237	150.9	0.22	0.14
425	1133.9	198.2	103.4	0.19	0.10
430	1147.3	173.6	71.7	0.16	0.07
435	1160.6	150.5	53	0.14	0.05
440	1174.0	130.5	38.8	0.12	0.04
445	1187.3	112.4	30.3	0.11	0.03
450	1200.6	97.6	25	0.09	0.02
455	1214.0	86.5	21.2	0.08	0.02
460	1227.3	73.5	18.1	0.07	0.02
465	1240.7	67	17.6	0.06	0.02
470	1254.0	54.6	15.7	0.05	0.01
475	1267.3	45.9	13.9	0.04	0.01
480	1280.7	38	12.7	0.04	0.01
485	1294.0	33.1	14.5	0.03	0.01
490	1307.4	27.6	11.6	0.03	0.01
495	1320.7	21	11	0.02	0.01
500	1334.1	20.4	10.2	0.02	0.01
505	1347.4	16.3	9.9	0.02	0.01
510	1360.7	14.1	9.3	0.01	0.01
515	1374.1	13.5	9	0.01	0.01
520	1387.4	11.5	8.6	0.01	0.01
525	1400.8	10.4	8.4	0.01	0.01
530	1414.1	10.1	7.9	0.01	0.01
535	1427.4	9.3	7.7	0.01	0.01
540	1440.8	8.9	7.7	0.01	0.01

Table C-2: Experiment 2: Formate break through and wash out curves from Elverum soil samples, Inlet EC=670 µS/cm

Time (mins)	EC A (µS/cm)	EC B (µS/cm)	Accumulative Volume (ml)		C/Co	
			A	B	A	B
0.0	5.6	5.5	26.94	27.00	0.01	0.01
10.0	5.0	6.4	52.74	53.20	0.01	0.01
20.0	4.9	4.9	74.67	78.83	0.01	0.01
30.0	4.7	4.8	101.73	106.29	0.01	0.01
40.0	4.6	4.7	125.51	133.77	0.01	0.01
50.0	4.5	4.6	152.24	160.90	0.01	0.01
60.0	4.4	4.5	175.89	188.27	0.01	0.01
70.0	4.3	4.6	202.89	215.67	0.01	0.01
80.0	4.3	4.6	226.23	242.71	0.01	0.01
90.0	112.1	56.8	253.34	270.22	0.17	0.08
100.0	134.6	223.0	277.04	297.62	0.20	0.33
110.0	242.0	309.0	303.88	324.86	0.36	0.46
120.0	377.0	357.0	327.78	352.46	0.56	0.53
130.0	429.0	462.0	354.48	379.56	0.64	0.69
140.0	456.0	503.0	378.27	407.05	0.68	0.75
150.0	477.0	521.0	405.18	434.36	0.71	0.78
160.0	493.0	526.0	428.90	461.78	0.74	0.79
170.0	511.0	532.0	455.68	488.96	0.76	0.79
180.0	518.0	521.0	479.12	516.10	0.77	0.78
190.0	522.0	523.0	506.34	543.72	0.78	0.78
200.0	530.0	536.0	530.11	571.19	0.79	0.80
210.0	531.0	544.0	557.23	598.71	0.79	0.81
220.0	545.0	551.0	580.89	626.07	0.81	0.82
230.0	550.0	562.0	607.78	653.36	0.82	0.84
240.0	564.0	572.0	631.30	680.58	0.84	0.85
250.0	564.0	578.0	658.33	708.01	0.84	0.86
260.0	577.0	580.0	682.15	735.53	0.86	0.87
270.0	576.0	595.0	709.62	763.40	0.86	0.89
280.0	589.0	602.0	736.16	790.65	0.88	0.90
290.0	607.0	589.0	764.17	817.92	0.91	0.88
300.0	603.0	619.0	790.11	844.57	0.90	0.92
310.0	612.0	628.0	817.92	872.35	0.91	0.94
320.0	609.0	626.0	843.72	899.55	0.91	0.93
330.0	632.0	617.0	869.52	926.05	0.94	0.92
340.0	611.0	638.0	896.01	953.26	0.91	0.95
350.0	620.0	645.0	922.87	980.78	0.93	0.96

360.0	626.0	643.0	949.55	1008.27	0.93	0.96
370.0	636.0	640.0	976.24	1035.70	0.95	0.96
380.0	636.0	655.0	1002.99	1063.20	0.95	0.98
390.0	643.0	650.0	1029.00	1089.89	0.96	0.97
400.0	640.0	650.0	1055.56	1117.08	0.96	0.97
410.0	641.0	652.0	1082.17	1144.71	0.96	0.97
420.0	649.0	650.0	1108.74	1171.91	0.97	0.97
430.0	647.0	653.0	1135.44	1199.41	0.97	0.97
440.0	650.0	655.0	1162.62	1227.46	0.97	0.98
450.0	647.0	664.0	1189.29	1254.86	0.97	0.99
460.0	650.0	661.0	1216.40	1282.96	0.97	0.99
470.0	653.0	652.0	1243.10	1310.46	0.97	0.97
480.0	650.0	650.0	1269.55	1337.60	0.97	0.97
490.0	654.0	659.0	1296.25	1365.20	0.98	0.98
500.0	653.0	656.0	1322.74	1392.30	0.97	0.98
510.0	650.0	660.0	1349.34	1419.80	0.97	0.99
520.0	653.0	665.0	1374.71	1447.00	0.97	0.99
530.0	661.0	663.0	1401.41	1474.40	0.99	0.99
540.0	658.0	664.0	1426.81	1501.60	0.98	0.99
550.0	649.0	653.0	1453.61	1529.30	0.97	0.97
560.0	575.0	614.0	1479.11	1556.30	0.86	0.92
570.0	430.0	529.0	1505.81	1582.40	0.64	0.79
580.0	318.0	321.0	1532.91	1611.90	0.47	0.48
590.0	230.0	268.0	1559.61	1637.40	0.34	0.40
600.0	151.4	123.7	1586.01	1664.50	0.23	0.18
610.0	103.0	49.6	1612.71	1692.10	0.15	0.07
620.0	70.0	23.2	1639.21	1719.20	0.10	0.03
630.0	50.3	16.0	1666.01	1746.70	0.08	0.02
640.0	36.9	12.2	1692.01	1773.90	0.06	0.02
650.0	26.5	9.7	1719.51	1801.30	0.04	0.01
660.0	18.6	8.7	1744.91	1828.50	0.03	0.01
670.0	13.2	7.6	1771.71	1856.20	0.02	0.01
680.0	9.5	6.8	1797.21	1883.20	0.01	0.01
690.0	7.3	6.1	1823.91	1909.30	0.01	0.01
700.0	6.5	5.6	1849.41	1938.80	0.01	0.01
710.0	6.3	5.4	1876.21	1964.30	0.01	0.01
720.0	6.2	5.3	1901.71	1993.80	0.01	0.01

Table C-3 :Experiment 2, COD analysis

Time (min)	Accumulative Volume (ml)		C/Co		COD (mg/lt)	
	A	B	A	B	A	B
60	175.9	188.3	0.01	0.01	-0.4	-0.9
90	253.3	270.2	0.17	0.08	11.4	4.1
120	327.8	352.5	0.56	0.53	39.0	37.0
180	479.1	516.1	0.77	0.78	54.1	53.0
450	1189.3	1254.9	0.97	0.99	53.1	58.9
570	1505.8	1582.4	0.64	0.79	34.3	43.0
600	1586.0	1664.5	0.23	0.18	5.3	12.3
630	1666.0	1746.7	0.08	0.02	1.3	0.6
690	1823.9	1909.3	0.01	0.01	-5.0	-1.0

Table C-4: Experiment 1 and 2, Comparison of NaCl / Formate elution through Elverum soil samples

Elverum Soil Columns						
NaCl			Formate			
Accumulative Volume (ml)	C/Co		Accumulative Volume (ml)		C/Co	
	A	B	A	B	A	B
0.00	0.14	0.14	26.94	27	0.01	0.01
13.34	0.12	0.13	52.74	53.2	0.01	0.01
26.68	0.11	0.12	74.67	78.83	0.01	0.01
40.02	0.10	0.10	101.73	106.29	0.01	0.01
53.36	0.09	0.09	125.51	133.77	0.01	0.01
66.70	0.08	0.08	152.24	160.9	0.01	0.01
80.04	0.07	0.07	175.89	188.27	0.01	0.01
93.38	0.07	0.06	202.89	215.67	0.01	0.01
106.72	0.06	0.05	226.23	242.71	0.01	0.01
120.06	0.05	0.04	253.34	270.22	0.17	0.08
133.41	0.05	0.04	277.04	297.62	0.20	0.33
146.75	0.04	0.03	303.88	324.86	0.36	0.46
160.09	0.04	0.03	327.78	352.46	0.56	0.53
173.43	0.04	0.03	354.48	379.56	0.64	0.69
186.77	0.03	0.03	378.27	407.05	0.68	0.75
200.11	0.05	0.03	405.18	434.36	0.71	0.78
213.45	0.03	0.02	428.9	461.78	0.74	0.79
226.79	0.03	0.02	455.68	488.96	0.76	0.79
240.13	0.03	0.02	479.12	516.1	0.77	0.78

253.47	0.03	0.02	506.34	543.72	0.78	0.78
266.81	0.04	0.02	530.11	571.19	0.79	0.80
280.15	0.09	0.03	557.23	598.71	0.79	0.81
293.49	0.16	0.06	580.89	626.07	0.81	0.82
306.83	0.25	0.13	607.78	653.36	0.82	0.84
320.17	0.36	0.24	631.3	680.58	0.84	0.85
333.51	0.45	0.36	658.33	708.01	0.84	0.86
346.85	0.53	0.46	682.15	735.53	0.86	0.87
360.19	0.60	0.55	709.62	763.4	0.86	0.89
373.53	0.65	0.64	736.16	790.65	0.88	0.90
386.87	0.71	0.72	764.17	817.92	0.91	0.88
400.22	0.75	0.78	790.11	844.57	0.90	0.92
413.56	0.78	0.83	817.92	872.35	0.91	0.94
426.90	0.81	0.87	843.72	899.55	0.91	0.93
440.24	0.84	0.92	869.52	926.05	0.94	0.92
453.58	0.86	0.95	896.01	953.26	0.91	0.95
466.92	0.88	0.97	922.87	980.78	0.93	0.96
480.26	0.90	0.99	949.55	1008.27	0.93	0.96
493.60	0.92	1.00	976.24	1035.7	0.95	0.96
506.94	0.93	1.00	1002.99	1063.2	0.95	0.98
520.28	0.94	1.01	1029	1089.89	0.96	0.97
533.62	0.95	1.01	1055.56	1117.08	0.96	0.97
546.96	0.96	1.01	1082.17	1144.71	0.96	0.97
560.30	0.96	1.01	1108.74	1171.91	0.97	0.97
573.64	0.97	1.01	1135.44	1199.41	0.97	0.97
586.98	0.98	1.01	1162.62	1227.46	0.97	0.98
600.32	0.99	1.01	1189.29	1254.86	0.97	0.99
613.66	0.99	1.01	1216.4	1282.96	0.97	0.99
627.00	1.00	1.01	1243.1	1310.46	0.97	0.97
640.34	1.01	1.02	1269.55	1337.6	0.97	0.97
653.68	1.01	1.02	1296.25	1365.2	0.98	0.98
667.03	1.01	1.02	1322.74	1392.3	0.97	0.98
680.37	1.01	1.01	1349.34	1419.8	0.97	0.99
693.71	1.01	1.01	1374.71	1447	0.97	0.99
707.05	1.02	1.02	1401.41	1474.4	0.99	0.99
720.39	1.03	1.02	1426.81	1501.6	0.98	0.99
733.73	1.02	1.03	1453.61	1529.3	0.97	0.97
747.07	1.03	1.02	1479.11	1556.3	0.86	0.92
760.41	1.03	1.02	1505.81	1582.4	0.64	0.79
773.75	1.03	1.02	1532.91	1611.9	0.47	0.48
787.09	1.03	1.02	1559.61	1637.4	0.34	0.40

800.43	1.03	1.02	1586.01	1664.5	0.23	0.18
813.77	1.03	1.02	1612.71	1692.1	0.15	0.07
827.11	1.03	1.02	1639.21	1719.2	0.10	0.03
840.45	1.03	1.02	1666.01	1746.7	0.08	0.02
853.79	1.02	1.02	1692.01	1773.9	0.06	0.02
867.13	1.02	1.01	1719.51	1801.3	0.04	0.01
880.47	1.01	1.01	1744.91	1828.5	0.03	0.01
893.81	1.01	1.01	1771.71	1856.2	0.02	0.01
907.15	1.01	1.01	1797.21	1883.2	0.01	0.01
920.49	1.01	1.01	1823.91	1909.3	0.01	0.01
933.84	1.01	1.01	1849.41	1938.8	0.01	0.01
947.18	1.02	1.01	1876.21	1964.3	0.01	0.01
960.52	1.02	1.01	1901.71	1993.8	0.01	0.01
973.86	1.01	1.01				
987.20	0.99	1.00				
1000.54	0.90	0.95				
1013.88	0.80	0.88				
1027.22	0.69	0.77				
1040.56	0.59	0.66				
1053.90	0.50	0.55				
1067.24	0.43	0.45				
1080.58	0.36	0.35				
1093.92	0.29	0.26				
1107.26	0.25	0.19				
1120.60	0.22	0.14				
1133.94	0.19	0.10				
1147.28	0.16	0.07				
1160.62	0.14	0.05				
1173.96	0.12	0.04				
1187.30	0.11	0.03				
1200.65	0.09	0.02				
1213.99	0.08	0.02				
1227.33	0.07	0.02				
1240.67	0.06	0.02				
1254.01	0.05	0.01				
1267.35	0.04	0.01				
1280.69	0.04	0.01				
1294.03	0.03	0.01				
1307.37	0.03	0.01				
1320.71	0.02	0.01				
1334.05	0.02	0.01				

1347.39	0.02	0.01				
1360.73	0.01	0.01				
1374.07	0.01	0.01				
1387.41	0.01	0.01				
1400.75	0.01	0.01				
1414.09	0.01	0.01				
1427.43	0.01	0.01				
1440.77	0.01	0.01				

Table C-5 : Experiment 3 Time step , Elverum soil samples elution with Formate

Time (days)	Description	VOL (lt)	EC (µS/cm)		C/Co		COD (mg/lt)		
			A	B	A	B	In	A	B
4		0.7	568	586	0.83	0.86			
5		1.3	642	628	0.94	0.92			
6		2.0	639	628	0.94	0.92			
7		2.6	642	632	0.94	0.93			
8		3.3	655	643	0.96	0.94			
11	**Change of flow**	5.2	650	634	0.95	0.93	45.6	37.1	38.6
12		6.0	666	658	0.98	0.96			
13		6.8	663	673	0.97	0.99			
14		7.6	670	668	0.98	0.98			
15		8.3	664	661	0.97	0.97			
18	**Change of flow**	10.7	633	630	0.93	0.92	53.3	53.8	34.0
19		12.3	677	682	1.00	1.01			
20		14.0	685	701	1.02	1.04			
21		15.7	655	673	1.00	1.00			
22		17.3	647	645	0.96	0.96			
25	**Change of flow**	22.4	696	687	1.00	0.99	43.2	45.5	47.9
26		24.8	700	704	1.00	1.01			
27		27.3	684	687	0.98	0.99			
28		29.8	678	681	0.98	0.98			
29		32.3	674	682	1.00	1.00			
32	**Change of flow**	39.7	690	689	1.01	1.01	49.7	46.0	47.6
33		43.2	689	687	1.00	0.99			
34		46.7	695	695	1.00	1.00			
35		50.2	691	693	1.00	1.01			
36		53.7	689	691	1.00	1.00			
39	**Change of flow**	64.2	687	690	1.00	1.00	53.3	46.0	46.9
40		68.7	689	683	1.00	0.99			
41		73.2	683	684	0.99	0.99			
42		77.7	676	681	0.98	0.99			
43	**End of Experiment**	82.2	682	684	0.99	0.99	50.5	46.9	45.8

Table C-6: Experiment 4, NaCl breakthrough and wash out curves from OSL soil columns, Inlet EC= 540 µS/cm

Time (min)	Accumulative Volume (ml)		EC (µS/cm		C/Co	
	A	B	A	B	A	B
0	0.0	0.0				
10	6.3	5.9	13.9	12.1	0.03	0.02
20	12.4	13.1	12.9	11.5	0.02	0.02
30	15.8	19.9	9.7	12.9	0.02	0.02
40	19.7	25.6	4	13	0.01	0.02
50	25.1	32.4	12.2	13.3	0.02	0.02
60	31.1	38.9	14.4	13.7	0.03	0.03
70	37.3	45.0	14.5	13.6	0.03	0.03
80	43.2	51.3	14.6	24.4	0.03	0.05
90	49.3	57.4	14.7	27.1	0.03	0.05
100	56.3	64.7	14.9	31.7	0.03	0.06
110	63.2	71.4	16.3	58.6	0.03	0.11
120	71.6	78.3	18.9	71.3	0.04	0.13
130	79.9	85.4	20.2	82.8	0.04	0.15
140	85.8	91.2	31.4	94.9	0.06	0.18
150	91.8	97.1	48.4	110.8	0.09	0.21
160	97.9	103.1	67.9	121.9	0.13	0.23
170	103.7	108.9	100.3	168.6	0.19	0.31
180	109.7	115.0	127.1	199.9	0.24	0.37
190	115.8	121.2	150	247	0.28	0.46
200	121.8	127.2	182.5	282	0.34	0.52
210	128.0	133.1	195	301	0.36	0.56
220	134.0	139.1	211	325	0.39	0.60
230	140.1	145.2	229	330	0.42	0.61
240	146.1	151.3	249	339	0.46	0.63
250	152.1	157.6	254	337	0.47	0.62
260	158.2	163.8	279	323	0.52	0.60
270	164.2	169.9	284	314	0.53	0.58
280	170.3	176.2	297	307	0.55	0.57
290	176.4	182.5	301	314	0.56	0.58
300	182.5	188.8	309	318	0.57	0.59
310	188.5	195.1	311	320	0.58	0.59
320	194.7	201.3	323	324	0.60	0.60
330	200.9	207.6	329	320	0.61	0.59

340	207.2	213.9	336	318	0.62	0.59
350	213.5	220.1	340	315	0.63	0.58
360	219.8	226.4	348	294	0.64	0.54
370	226.1	232.6	353	291	0.65	0.54
380	232.4	238.9	364	287	0.67	0.53
390	238.7	245.1	371	286	0.69	0.53
400	245.0	251.3	375	284	0.69	0.53
410	251.2	257.5	386	284	0.71	0.53
420	257.3	263.6	393	283	0.73	0.52
430	263.4	269.8	399	290	0.74	0.54
440	269.6	276.0	404	292	0.75	0.54
450	275.7	282.1	405	293	0.75	0.54
460	281.8	288.3	417	297	0.77	0.55
470	288.0	294.5	423	300	0.78	0.56
480	294.1	300.7	421	309	0.78	0.57
490	300.3	306.9	420	310	0.78	0.57
500	306.4	313.1	419	314	0.78	0.58
510	312.6	319.3	421	327	0.78	0.61
520	318.8	325.5	434	331	0.80	0.61
530	324.9	331.7	440	334	0.81	0.62
540	331.1	338.0	440	334	0.81	0.62
550	337.3	344.2	443	339	0.82	0.63
560	343.5	350.4	444	341	0.82	0.63
570	349.6	356.6	448	349	0.83	0.65
580	355.8	362.9	450	353	0.83	0.65
590	362.0	369.1	453	357	0.84	0.66
600	368.2	375.3	453	370	0.84	0.69
610	374.4	381.5	454	369	0.84	0.68
620	380.6	387.7	455	373	0.84	0.69
630	386.8	393.9	457	376	0.85	0.70
640	393.0	400.1	461	381	0.85	0.71
650	399.2	406.3	466	386	0.86	0.71
660	405.3	412.5	460	390	0.85	0.72
670	411.5	418.7	456	395	0.84	0.73
680	417.7	424.9	457	401	0.85	0.74
690	423.9	431.1	459	403	0.85	0.75
700	430.0	437.3	467	410	0.86	0.76
710	436.2	443.5	480	414	0.89	0.77
720	442.4	449.7	491	436	0.91	0.81
2160	1543.9	1589.3	554	555	1.03	1.03
2170	1550.8	1596.1	555	556	1.03	1.03

2180	1557.9	1603.5	553	557	1.02	1.03
2190	1564.9	1611.1	551	556	1.02	1.03
2200	1571.8	1618.1	550	555	1.02	1.03
2210	1577.9	1624.6	549	554	1.02	1.03
2220	1584.5	1631.3	541	555	1.00	1.03
2230	1590.9	1637.8	534	556	0.99	1.03
2240	1597.4	1644.4	505	550	0.94	1.02
2250	1603.8	1651.0	481	548	0.89	1.01
2260	1610.5	1657.8	454	550	0.84	1.02
2270	1617.1	1664.5	431	549	0.80	1.02
2280	1623.6	1671.2	391	545	0.72	1.01
2290	1630.4	1678.1	368	547	0.68	1.01
2300	1637.0	1684.9	352	541	0.65	1.00
2310	1643.5	1691.6	321	538	0.59	1.00
2320	1650.3	1698.5	318	536	0.59	0.99
2330	1657.2	1705.5	301	528	0.56	0.98
2340	1663.8	1712.1	287	514	0.53	0.95
2350	1670.3	1718.8	276	505	0.51	0.94
2360	1677.0	1725.6	265	500	0.49	0.93
2370	1683.6	1732.3	257	491	0.48	0.91
2380	1690.2	1739.1	247	467	0.46	0.86
2390	1696.7	1745.7	239	436	0.44	0.81
2400	1703.4	1752.6	240	428	0.44	0.79
2410	1709.9	1759.3	243	418	0.45	0.77
2420	1716.3	1765.9	242	397	0.45	0.74
2430	1723.0	1772.8	245	371	0.45	0.69
2440	1729.6	1779.5	246	354	0.46	0.66
2450	1736.1	1786.1	247	335	0.46	0.62
2460	1742.9	1793.1	233	298	0.43	0.55
2470	1749.8	1800.1	244	327	0.45	0.61
2480	1756.6	1807.1	243	325	0.45	0.60
2490	1763.5	1814.1	240	321	0.44	0.59
2500	1770.2	1820.9	236	310	0.44	0.57
2510	1777.0	1827.8	230	298	0.43	0.55
2520	1783.8	1834.7	231	281	0.43	0.52
2530	1790.7	1841.7	238	274	0.44	0.51
2540	1797.4	1848.6	249	276	0.46	0.51
2550	1804.1	1855.4	252	279	0.47	0.52
2560	1810.9	1862.3	269	263	0.50	0.49
2570	1817.5	1869.1	273	255	0.51	0.47
2580	1824.2	1875.8	279	236	0.52	0.44

2590	1831.0	1882.7	298	219	0.55	0.41
2600	1837.7	1889.5	301	205	0.56	0.38
2610	1844.6	1896.5	305	190.5	0.56	0.35
2620	1851.0	1903.1	302	181.3	0.56	0.34
2630	1857.3	1909.7	293	168.4	0.54	0.31
2640	1863.9	1916.4	291	155.9	0.54	0.29
2650	1870.6	1923.3	275	148.8	0.51	0.28
2660	1877.3	1930.2	263	141.3	0.49	0.26
2670	1883.9	1936.9	252	136.8	0.47	0.25
2680	1890.4	1943.6	241	142.1	0.45	0.26
2690	1896.9	1950.3	230	139.1	0.43	0.26
2700	1903.5	1957.1	219	139.6	0.41	0.26
2710	1910.1	1963.7	216	138.5	0.40	0.26
2720	1916.8	1970.6	201	137	0.37	0.25
2730	1923.3	1977.2	197.7	136.9	0.37	0.25
2740	1929.9	1984.0	186.2	135.8	0.34	0.25
2750	1936.3	1990.6	179.2	135.2	0.33	0.25
2760	1943.0	1997.5	163.4	136.6	0.30	0.25
2770	1949.6	2004.2	159.9	136.4	0.30	0.25
2780	1956.4	2011.1	144.9	136.4	0.27	0.25
2790	1963.3	2018.0	136.1	136.2	0.25	0.25
2800	1970.0	2024.8	140.2	134.6	0.26	0.25
2810	1976.8	2031.8	143.1	131.2	0.27	0.24
2820	1983.6	2038.7	142.1	132.3	0.26	0.25
2830	1990.2	2045.5	143.5	131.5	0.27	0.24
2840	1997.0	2052.5	141.6	129.3	0.26	0.24
2850	2003.7	2059.3	140.2	124.5	0.26	0.23
2860	2010.5	2066.3	139.1	124.9	0.26	0.23
2870	2017.1	2073.1	134	123.7	0.25	0.23
2880	2023.6	2079.8	123	125.6	0.23	0.23
2890	2030.2	2086.5	117.9	125.4	0.22	0.23
2900	2036.9	2093.3	113.7	127.7	0.21	0.24
2910	2043.5	2100.1	108.7	109.4	0.20	0.20
2920	2050.0	2106.7	105.3	97.4	0.20	0.18
2930	2056.6	2113.4	104.1	98.9	0.19	0.18
2940	2063.1	2120.1	103.5	96.5	0.19	0.18
2950	2069.6	2126.9	100.7	95.8	0.19	0.18

Table C-7: Experiment 5, Formate break through and wash out curves with OSL columns

Time (min)	EC (µS/cm)		C/Co		Accumulative Volume (ml)	
	A	B	A	B	A	B
10	24	15	0.04	0.02	7.5	7.5
20	21.3	18.2	0.03	0.03	14.2	14.3
30	20.2	21	0.03	0.03	20.7	20.8
40	20.3	19.7	0.03	0.03	27.4	27.8
50	20.3	18.3	0.03	0.03	33.9	34.7
60	18.3	16.2	0.03	0.02	40.7	41.7
70	16.3	19.3	0.02	0.03	47.7	48.8
80	17.9	20	0.03	0.03	54.3	55.6
90	18.8	20.2	0.03	0.03	60.8	61.9
100	13.3	16.9	0.02	0.03	67.2	68.4
110	16.1	13	0.02	0.02	72.2	73.9
120	20.5	12.8	0.03	0.02	78.2	80.4
130	17.5	19.8	0.03	0.03	84.4	86.9
140	16.9	14.2	0.03	0.02	90.3	92.9
150	19.6	18	0.03	0.03	95.3	98.4
160	19.9	14.1	0.03	0.02	101.1	104.4
170	15.9	13.8	0.02	0.02	106.1	109.4
180	16.5	13.8	0.03	0.02	112.6	115.9
190	19.5	13.5	0.03	0.02	117.6	120.9
200	21.7	21.6	0.03	0.03	123.1	126.9
210	25.3	23.7	0.04	0.04	129.6	133.4
220	25.6	25.5	0.04	0.04	135.5	139.4
230	25	27.2	0.04	0.04	141.5	145.6
240	26.4	30.5	0.04	0.05	147.7	151.9
250	27.1	31.7	0.04	0.05	153.2	157.9
260	29.5	37.3	0.04	0.06	159.2	164.1
270	27.2	36.6	0.04	0.06	165.3	170.4
280	30.6	43.5	0.05	0.07	171	176.4
290	37.7	49.9	0.06	0.08	177.1	182.7
300	41.9	51.7	0.06	0.08	183.1	188.7
310	48.6	84.1	0.07	0.13	189.1	194.8
320	51	72.5	0.08	0.11	195.3	201.1
330	54.7	80.7	0.08	0.12	201.3	207.2
340	60.1	89.7	0.09	0.14	207.4	213.5
350	61.4	95.5	0.09	0.14	213.4	219.7
360	71.1	103	0.11	0.16	219.3	225.7
370	71.3	112	0.11	0.17	225.3	231.9
380	76	116.4	0.12	0.18	231.2	237.9

390	82.8	125.4	0.13	0.19	237.2	243.9
400	88.6	130.8	0.13	0.20	243.3	250.1
410	87.4	127.6	0.13	0.19	249.2	256.1
420	99.1	144.7	0.15	0.22	254.7	262.1
430	103.3	147.2	0.16	0.22	260.5	268.1
440	107.9	152	0.16	0.23	266.5	274.2
450	115.1	156.1	0.17	0.24	272.5	280.3
460	114.7	149.9	0.17	0.23	278.5	286.5
470	123.8	169.1	0.19	0.26	284.5	292.6
480	131.8	176.6	0.20	0.27	290.5	298.8
490	135	181.3	0.20	0.27	296.5	304.9
500	142.5	185.8	0.22	0.28	302.5	311
510	118.9	188.4	0.18	0.29	308.5	317.1
520	143	199.3	0.22	0.30	313.5	322.1
530	155.4	205	0.24	0.31	319.5	328.2
540	153.3	209	0.23	0.32	325.5	334.4
550	166.7	227	0.25	0.34	331.5	340.5
560	178.4	230	0.27	0.35	337.4	346.5
570	177.9	221	0.27	0.33	343.4	352.7
580	188.3	241	0.29	0.37	349.4	358.8
590	195.6	262	0.30	0.40	355.5	365.1
600	205	268	0.31	0.41	361.8	371.5
610	234	272	0.35	0.41	367.8	377.6
620	231	274	0.35	0.42	373.8	383.7
630	244	266	0.37	0.40	379.8	389.8
640	251	288	0.38	0.44	385.9	396.1
650	267	291	0.40	0.44	392.2	402.5
660	282	309	0.43	0.47	398.3	408.7
670	276	319	0.42	0.48	404.5	415
680	291	343	0.44	0.52	410.5	421.4
690	329	390	0.50	0.59	417.2	428
700	325	404	0.49	0.61	423.3	434.3
710	314	382	0.48	0.58	429.6	440.8
720	331	401	0.50	0.61	436.2	447.6
730	334	391	0.51	0.59	442.1	453.6
740	315	382	0.48	0.58	448.1	459.7
750	329	382	0.50	0.58	454.2	465.9
760	325	401	0.49	0.61	460.6	472.4
770	330	403	0.50	0.61	467.2	479.2
780	327	409	0.50	0.62	473.9	486
2820	580	596	0.88	0.90	1712.2	1756.9

2830	580	596	0.88	0.90	1718.3	1763.1
2840	590	599	0.89	0.91	1724.3	1769.2
2850	597	601	0.90	0.91	1730.4	1775.5
2860	597	601	0.90	0.91	1736.4	1781.6
2870	596	603	0.90	0.91	1742.4	1787.7
2880	595	599	0.90	0.91	1748.7	1794.0
2890	603	611	0.91	0.93	1755.2	1800.6
2900	597	605	0.90	0.92	1761.8	1807.3
2910	591	603	0.90	0.91	1768.4	1813.8
2920	598	603	0.91	0.91	1775.0	1820.4
2930	597	602	0.90	0.91	1781.8	1827.4
2940	597	605	0.90	0.92	1788.1	1833.8
2950	595	606	0.90	0.92	1794.7	1840.6
2960	593	603	0.90	0.91	1801.2	1847.5
2970	591	602	0.90	0.91	1807.6	1854.1
2980	590	604	0.89	0.92	1813.6	1860.2
2990	588	605	0.89	0.92	1820.4	1867.2
3000	581	605	0.88	0.92	1826.7	1873.7
3010	574	607	0.87	0.92	1833.2	1880.3
3020	561	606	0.85	0.92	1839.5	1886.8
3030	554	604	0.84	0.92	1846.0	1893.4
3040	543	595	0.82	0.90	1852.0	1899.5
3050	536	599	0.81	0.91	1858.2	1905.5
3060	517	602	0.78	0.91	1864.5	1911.9
3070	513	605	0.78	0.92	1871.0	1918.5
3080	510	604	0.77	0.92	1877.6	1925.3
3090	501	603	0.76	0.91	1883.9	1931.8
3100	488	603	0.74	0.91	1889.9	1937.8
3110	455	602	0.69	0.91	1896.4	1944.5
3120	450	601	0.68	0.91	1903.0	1951.3
3130	446	596	0.68	0.90	1909.6	1957.9
3140	437	588	0.66	0.89	1916.0	1964.4
3150	428	580	0.65	0.88	1922.5	1971.0
3160	415	576	0.63	0.87	1929.1	1977.9
3170	404	570	0.61	0.86	1935.6	1984.5
3180	399	543	0.60	0.82	1942.1	1991.2
3190	396	551	0.60	0.83	1948.6	1998.2
3200	388	545	0.59	0.83	1955.2	2005.0
3210	377	531	0.57	0.80	1961.7	2011.6
3220	384	524	0.58	0.79	1968.2	2018.2
3230	391	516	0.59	0.78	1974.8	2024.9

3240	361	509	0.55	0.77	1981.3	2031.5
3250	399	500	0.60	0.76	1988.1	2038.5
3260	331	493	0.50	0.75	1995.1	2045.5
3270	325	481	0.49	0.73	2001.9	2052.5
3280	326	468	0.49	0.71	2007.9	2058.5
3290	317	463	0.48	0.70	2014.2	2064.6
3300	306	464	0.46	0.70	2020.6	2071.3
3310	297	455	0.45	0.69	2027.1	2078.0
3320	284	446	0.43	0.68	2033.7	2084.7
3330	275	439	0.42	0.67	2040.0	2091.2
3340	262	428	0.40	0.65	2046.5	2097.9
3350	247	424	0.37	0.64	2051.5	2103.9
3360	263	421	0.40	0.64	2057.8	2110.4
3370	252	418	0.38	0.63	2064.5	2117.3
3380	247	415	0.37	0.63	2070.7	2123.6
3390	243	401	0.37	0.61	2077.2	2130.2
3400	236	394	0.36	0.60	2083.5	2136.7
3410	227	388	0.34	0.59	2090.0	2143.4
3420	215	370	0.33	0.56	2096.0	2149.4
3430	212	370	0.32	0.56	2102.2	2155.4
3440	209	356	0.32	0.54	2108.5	2162.0
3450	204	348	0.31	0.53	2115.0	2168.7
3460	199.7	349	0.30	0.53	2121.3	2175.2
3470	176.1	347	0.27	0.53	2127.9	2182.1
3480	186.1	340	0.28	0.52	2134.2	2188.6
3490	186.9	334	0.28	0.51	2140.7	2195.2
3500	180.7	333	0.27	0.50	2147.3	2201.9
3510	176.5	331	0.27	0.50	2153.7	2208.5
3520	170.3	325	0.26	0.49	2160.2	2215.1
3530	164.9	317	0.25	0.48	2166.8	2221.8
3540	157.6	312	0.24	0.47	2173.1	2228.3
3550	148.1	307	0.22	0.47	2179.7	2235.2
3560	148.6	298	0.23	0.45	2186.7	2242.7
3570	146.3	290	0.22	0.44	2193.2	2249.3
3580	146.2	277	0.22	0.42	2199.8	2256.2
3590	143	266	0.22	0.40	2205.9	2263.1
3600	133.2	264	0.20	0.40	2212.2	2269.2
3610	131.6	266	0.20	0.40	2219.1	2276.0
3620	129.6	260	0.20	0.39	2225.1	2282.3

Table C-8: Experiment 5, COD analysis

Accumulative Volume (ml)		C/Co		COD (mg/lt)	
A	B	A	B	A	B
60.8	61.9	0.03	0.03	13.9	9.9
183.1	188.7	0.06	0.08	10.1	11.7
313.5	322.1	0.22	0.30	19.0	21.9
423.3	434.3	0.49	0.61	28.0	30.7
1748.7	1794.0	0.90	0.91	55.1	64.3
1896.4	1944.5	0.69	0.91	44.3	55.0
2007.9	2058.5	0.49	0.71	33.7	41.7
2096.0	2149.4	0.33	0.56	22.0	34.4
2225.1	2282.3	0.20	0.39	44.1	23.4

Table C-9 : Experiment 4 and 5, Comparison of Formate and NaCl Elution through OSL columns

Nacl				Formate			
Accululative Volume (ml)		C/Co		Accululative Volume (ml)		C/Co	
A	B	A	B	A	B	A	B
0	0			0	0		
6.3	5.9	0.03	0.02	7.5	7.5	0.04	0.02
12.4	13.1	0.02	0.02	14.2	14.3	0.03	0.03
15.8	19.9	0.02	0.02	20.7	20.8	0.03	0.03
19.7	25.6	0.01	0.02	27.4	27.8	0.03	0.03
25.1	32.4	0.02	0.02	33.9	34.7	0.03	0.03
31.1	38.9	0.03	0.03	40.7	41.7	0.03	0.02
37.3	45	0.03	0.03	47.7	48.8	0.02	0.03
43.2	51.3	0.03	0.05	54.3	55.6	0.03	0.03
49.3	57.4	0.03	0.05	60.8	61.9	0.03	0.03
56.3	64.7	0.03	0.06	67.2	68.4	0.02	0.03
63.2	71.4	0.03	0.11	72.2	73.9	0.02	0.02
71.6	78.3	0.04	0.13	78.2	80.4	0.03	0.02
79.9	85.4	0.04	0.15	84.4	86.9	0.03	0.03
85.8	91.2	0.06	0.18	90.3	92.9	0.03	0.02
91.8	97.1	0.09	0.21	95.3	98.4	0.03	0.03
97.9	103.1	0.13	0.23	101.1	104.4	0.03	0.02
103.7	108.9	0.19	0.31	106.1	109.4	0.02	0.02
109.7	115	0.24	0.37	112.6	115.9	0.03	0.02
115.8	121.2	0.28	0.46	117.6	120.9	0.03	0.02
121.8	127.2	0.34	0.52	123.1	126.9	0.03	0.03

128	133.1	0.36	0.56	129.6	133.4	0.04	0.04
134	139.1	0.39	0.60	135.5	139.4	0.04	0.04
140.1	145.2	0.42	0.61	141.5	145.6	0.04	0.04
146.1	151.3	0.46	0.63	147.7	151.9	0.04	0.05
152.1	157.6	0.47	0.62	153.2	157.9	0.04	0.05
158.2	163.8	0.52	0.60	159.2	164.1	0.04	0.06
164.2	169.9	0.53	0.58	165.3	170.4	0.04	0.06
170.3	176.2	0.55	0.57	171	176.4	0.05	0.07
176.4	182.5	0.56	0.58	177.1	182.7	0.06	0.08
182.5	188.8	0.57	0.59	183.1	188.7	0.06	0.08
188.5	195.1	0.58	0.59	189.1	194.8	0.07	0.13
194.7	201.3	0.60	0.60	195.3	201.1	0.08	0.11
200.9	207.6	0.61	0.59	201.3	207.2	0.08	0.12
207.2	213.9	0.62	0.59	207.4	213.5	0.09	0.14
213.5	220.1	0.63	0.58	213.4	219.7	0.09	0.14
219.8	226.4	0.64	0.54	219.3	225.7	0.11	0.16
226.1	232.6	0.65	0.54	225.3	231.9	0.11	0.17
232.4	238.9	0.67	0.53	231.2	237.9	0.12	0.18
238.7	245.1	0.69	0.53	237.2	243.9	0.13	0.19
245.0	251.3	0.69	0.53	243.3	250.1	0.13	0.20
251.2	257.5	0.71	0.53	249.2	256.1	0.13	0.19
257.3	263.6	0.73	0.52	254.7	262.1	0.15	0.22
263.4	269.8	0.74	0.54	260.5	268.1	0.16	0.22
269.6	276.0	0.75	0.54	266.5	274.2	0.16	0.23
275.7	282.1	0.75	0.54	272.5	280.3	0.17	0.24
281.8	288.3	0.77	0.55	278.5	286.5	0.17	0.23
288.0	294.5	0.78	0.56	284.5	292.6	0.19	0.26
294.1	300.7	0.78	0.57	290.5	298.8	0.20	0.27
300.3	306.9	0.78	0.57	296.5	304.9	0.20	0.27
306.4	313.1	0.78	0.58	302.5	311	0.22	0.28
312.6	319.3	0.78	0.61	308.5	317.1	0.18	0.29
318.8	325.5	0.80	0.61	313.5	322.1	0.22	0.30
324.9	331.7	0.81	0.62	319.5	328.2	0.24	0.31
331.1	338.0	0.81	0.62	325.5	334.4	0.23	0.32
337.3	344.2	0.82	0.63	331.5	340.5	0.25	0.34
343.5	350.4	0.82	0.63	337.4	346.5	0.27	0.35
349.6	356.6	0.83	0.65	343.4	352.7	0.27	0.33
355.8	362.9	0.83	0.65	349.4	358.8	0.29	0.37
362.0	369.1	0.84	0.66	355.5	365.1	0.30	0.40
368.2	375.3	0.84	0.69	361.8	371.5	0.31	0.41
374.4	381.5	0.84	0.68	367.8	377.6	0.35	0.41

380.6	387.7	0.84	0.69	373.8	383.7	0.35	0.42
386.8	393.9	0.85	0.70	379.8	389.8	0.37	0.40
393.0	400.1	0.85	0.71	385.9	396.1	0.38	0.44
399.2	406.3	0.86	0.71	392.2	402.5	0.40	0.44
405.3	412.5	0.85	0.72	398.3	408.7	0.43	0.47
411.5	418.7	0.84	0.73	404.5	415	0.42	0.48
417.7	424.9	0.85	0.74	410.5	421.4	0.44	0.52
423.9	431.1	0.85	0.75	417.2	428	0.50	0.59
430.0	437.3	0.86	0.76	423.3	434.3	0.49	0.61
436.2	443.5	0.89	0.77	429.6	440.8	0.48	0.58
442.4	449.7	0.91	0.81	436.2	447.6	0.50	0.61
1543.9	1589.3	1.03	1.03	442.1	453.6	0.51	0.59
1550.8	1596.1	1.03	1.03	448.1	459.7	0.48	0.58
1557.9	1603.5	1.02	1.03	454.2	465.9	0.50	0.58
1564.9	1611.1	1.02	1.03	460.6	472.4	0.49	0.61
1571.8	1618.1	1.02	1.03	467.2	479.2	0.50	0.61
1577.9	1624.6	1.02	1.03	473.9	486	0.50	0.62
1584.5	1631.3	1.00	1.03	1712.2	1756.9	0.88	0.90
1590.9	1637.8	0.99	1.03	1718.3	1763.1	0.88	0.90
1597.4	1644.4	0.94	1.02	1724.3	1769.2	0.89	0.91
1603.8	1651.0	0.89	1.01	1730.4	1775.5	0.90	0.91
1610.5	1657.8	0.84	1.02	1736.4	1781.6	0.90	0.91
1617.1	1664.5	0.80	1.02	1742.4	1787.7	0.90	0.91
1623.6	1671.2	0.72	1.01	1748.7	1794.0	0.90	0.91
1630.4	1678.1	0.68	1.01	1755.2	1800.6	0.91	0.93
1637.0	1684.9	0.65	1.00	1761.8	1807.3	0.90	0.92
1643.5	1691.6	0.59	1.00	1768.4	1813.8	0.90	0.91
1650.3	1698.5	0.59	0.99	1775.0	1820.4	0.91	0.91
1657.2	1705.5	0.56	0.98	1781.8	1827.4	0.90	0.91
1663.8	1712.1	0.53	0.95	1788.1	1833.8	0.90	0.92
1670.3	1718.8	0.51	0.94	1794.7	1840.6	0.90	0.92
1677.0	1725.6	0.49	0.93	1801.2	1847.5	0.90	0.91
1683.6	1732.3	0.48	0.91	1807.6	1854.1	0.90	0.91
1690.2	1739.1	0.46	0.86	1813.6	1860.2	0.89	0.92
1696.7	1745.7	0.44	0.81	1820.4	1867.2	0.89	0.92
1703.4	1752.6	0.44	0.79	1826.7	1873.7	0.88	0.92
1709.9	1759.3	0.45	0.77	1833.2	1880.3	0.87	0.92
1716.3	1765.9	0.45	0.74	1839.5	1886.8	0.85	0.92
1723.0	1772.8	0.45	0.69	1846.0	1893.4	0.84	0.92
1729.6	1779.5	0.46	0.66	1852.0	1899.5	0.82	0.90
1736.1	1786.1	0.46	0.62	1858.2	1905.5	0.81	0.91

1742.9	1793.1	0.43	0.55	1864.5	1911.9	0.78	0.91
1749.8	1800.1	0.45	0.61	1871.0	1918.5	0.78	0.92
1756.6	1807.1	0.45	0.60	1877.6	1925.3	0.77	0.92
1763.5	1814.1	0.44	0.59	1883.9	1931.8	0.76	0.91
1770.2	1820.9	0.44	0.57	1889.9	1937.8	0.74	0.91
1777.0	1827.8	0.43	0.55	1896.4	1944.5	0.69	0.91
1783.8	1834.7	0.43	0.52	1903.0	1951.3	0.68	0.91
1790.7	1841.7	0.44	0.51	1909.6	1957.9	0.68	0.90
1797.4	1848.6	0.46	0.51	1916.0	1964.4	0.66	0.89
1804.1	1855.4	0.47	0.52	1922.5	1971.0	0.65	0.88
1810.9	1862.3	0.50	0.49	1929.1	1977.9	0.63	0.87
1817.5	1869.1	0.51	0.47	1935.6	1984.5	0.61	0.86
1824.2	1875.8	0.52	0.44	1942.1	1991.2	0.60	0.82
1831.0	1882.7	0.55	0.41	1948.6	1998.2	0.60	0.83
1837.7	1889.5	0.56	0.38	1955.2	2005.0	0.59	0.83
1844.6	1896.5	0.56	0.35	1961.7	2011.6	0.57	0.80
1851.0	1903.1	0.56	0.34	1968.2	2018.2	0.58	0.79
1857.3	1909.7	0.54	0.31	1974.8	2024.9	0.59	0.78
1863.9	1916.4	0.54	0.29	1981.3	2031.5	0.55	0.77
1870.6	1923.3	0.51	0.28	1988.1	2038.5	0.60	0.76
1877.3	1930.2	0.49	0.26	1995.1	2045.5	0.50	0.75
1883.9	1936.9	0.47	0.25	2001.9	2052.5	0.49	0.73
1890.4	1943.6	0.45	0.26	2007.9	2058.5	0.49	0.71
1896.9	1950.3	0.43	0.26	2014.2	2064.6	0.48	0.70
1903.5	1957.1	0.41	0.26	2020.6	2071.3	0.46	0.70
1910.1	1963.7	0.40	0.26	2027.1	2078.0	0.45	0.69
1916.8	1970.6	0.37	0.25	2033.7	2084.7	0.43	0.68
1923.3	1977.2	0.37	0.25	2040.0	2091.2	0.42	0.67
1929.9	1984.0	0.34	0.25	2046.5	2097.9	0.40	0.65
1936.3	1990.6	0.33	0.25	2051.5	2103.9	0.37	0.64
1943.0	1997.5	0.30	0.25	2057.8	2110.4	0.40	0.64
1949.6	2004.2	0.30	0.25	2064.5	2117.3	0.38	0.63
1956.4	2011.1	0.27	0.25	2070.7	2123.6	0.37	0.63
1963.3	2018.0	0.25	0.25	2077.2	2130.2	0.37	0.61
1970.0	2024.8	0.26	0.25	2083.5	2136.7	0.36	0.60
1976.8	2031.8	0.27	0.24	2090.0	2143.4	0.34	0.59
1983.6	2038.7	0.26	0.25	2096.0	2149.4	0.33	0.56
1990.2	2045.5	0.27	0.24	2102.2	2155.4	0.32	0.56
1997.0	2052.5	0.26	0.24	2108.5	2162.0	0.32	0.54
2003.7	2059.3	0.26	0.23	2115.0	2168.7	0.31	0.53
2010.5	2066.3	0.26	0.23	2121.3	2175.2	0.30	0.53

2017.1	2073.1	0.25	0.23	2127.9	2182.1	0.27	0.53
2023.6	2079.8	0.23	0.23	2134.2	2188.6	0.28	0.52
2030.2	2086.5	0.22	0.23	2140.7	2195.2	0.28	0.51
2036.9	2093.3	0.21	0.24	2147.3	2201.9	0.27	0.50
2043.5	2100.1	0.20	0.20	2153.7	2208.5	0.27	0.50
2050.0	2106.7	0.20	0.18	2160.2	2215.1	0.26	0.49
2056.6	2113.4	0.19	0.18	2166.8	2221.8	0.25	0.48
2063.1	2120.1	0.19	0.18	2173.1	2228.3	0.24	0.47
2069.6	2126.9	0.19	0.18	2179.7	2235.2	0.22	0.47
				2186.7	2242.7	0.23	0.45
				2193.2	2249.3	0.22	0.44
				2199.8	2256.2	0.22	0.42
				2205.9	2263.1	0.22	0.40
				2212.2	2269.2	0.20	0.40
				2219.1	2276.0	0.20	0.40
				2225.1	2282.3	0.20	0.39

Table C-10 : Experiment 6, Time Step with Formate through OSL columns

Time	Accumulative Volume (lt)		EC(µS/cm)			C/Co		COD (mg/lt)	
(days)	A	B	In	A	B	A	B	A	B
0	0	0	670	48.4	32.2	0.07	0.05		
0.7	0.8	0.8	670	517	531	0.77	0.79		
1	1.0	1.0	670	564	586	0.84	0.87	41.6	42.1
4	3.5	3.6	750	636	694	0.85	0.93	58.1	51.3
5	4.2	4.4	697	627	658	0.90	0.94	46.6	46.1
6	4.9	5.1	697	603	641	0.87	0.92	44.6	41.4
7	5.8	6.0	697	566	615	0.81	0.88	41.6	48.3
8	6.6	6.8	862	741	783	0.86	0.91	41.4	44.0
11	9.0	9.3	862	666	698	0.77	0.81	34.3	13.8
12	9.7	10.1	862	636	677	0.74	0.79		
13	10.5	10.9	862	661	696	0.77	0.81		
14	11.3	11.7	862	669	676	0.78	0.78		
15	11.9	12.3	865	668	674	0.77	0.78	36.3	32.7
18	14.2	14.7	865	694	682	0.80	0.79	38.6	17.9
20	15.7	16.2	865	715	722	0.83	0.83	38.7	34.5
22	17.2	17.8	865	729	740	0.84	0.86	46.3	38.4
25	19.4	20.2	865	759	768	0.88	0.89		
27	20.9	21.8	865	777	776	0.90	0.90		
29	22.4	23.3	862	784	779	0.91	0.90		
32	24.7	25.7	893	785	776	0.88	0.87	42.2	36.1

Appendix D: Solution Standards

The reaction of K-Formate with oxygen can be written as

$4K\text{-}COOH + O_2 \rightarrow 4CO_2 + 2H2O + 4K$

It means one mole of O2 is required by 4 moles of K formate for its reaction

One mole of K-formate requires 0.25 moles of O_2

Now

The dissociation reaction of $NaNO_3$ can be written as

$2NaNO_3 \rightarrow 2Na + N2 + 3O_2$

It means 2 moles of $NaNO_3$ can give 3 moles of O_2

So

3 moles of O_2 are given by 2 moles of $NaNO_3$

1 mole mole of O_2 will be given by 2/3 moles of $NaNO_3$

And similarly

0.25 moles of O_2 will be given by 2*0.25/3 = 0.1675 moles of $NaNO_3$

Now as we know that the O_2 required by K formate is given off by $NaNO_3$

And

1 mole of K-formate requires = 0.1675 moles of NaNO3

We used

0.00625 moles/liter of K-formate to make a 50mg/lt COD solution

So

0.00625 moles of k-formate will require =0.1675*0.00625 = 0.001 moles of $NaNO_3$

Table D-1: Solution Standards

Substance	**Solution Standard**	**Amount (g/lt)**
NaCl	0.0341 moles/liter	2.0
K-Formate	0.00625 moles/liter	0.5257
$NaNO_3$	0.001 moles/liter	0.085